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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE ONE HUNDRED AND FIFTY-NINTH GENERAL MEETING of the Institution of Petroleum Technologists was held at the Royal Society of Arts, John Street, Adelphi, W.C., on Tuesday, October 9th, 1934. The President, Mr. T. DEWHURST, occupied the Chair.

The Secretary read the list of candidates nominated for membership, and the following list of members elected :—

As Members.—Maurice Alfred Banks, Frederick Challenger, Graham Edgar, Henry Alexander Hammick, Prof. Alexander Oliver Rankin, James Edward Southcombe, Francis Eric Austin Thompson, George Herbert Thornley, George Walter.

As Transfer to Members.—Henry Norman Bassett, Roland Edward Hales, Charles Vincent Hill, Percy Llewellyn Hunting, Walter Kay, Freidrich Sager, Horace Stephan Virgo, Alfred Samuel Wolfner.

As Associate Members.—Reginald Alfred Adamson, Edward Victor Corps, George Charles Gould, Stanley Melville Hannan, Arthur William Jarman, Robert Blythman Kerr, William Keith McGavin, Alexander Keith Ogston, Norman Harry Pitts, Philip Herbert Brigstock Trasler.

As Transfer to Associate Member.—Edward Lionel Moore.

As Students.—Herbert James William Braddick, Justus Friederich Clausen, James Richard Horth, Brian Orchard Lisle, Gerard van der Neut. Edward Reginald Palmer.

As Associate.—James Ellams, Frederick Melton Fisher, Fred Howett, Manuel Menendez, Robert Gower Reid.

STUDENTS' MEDAL AND PRIZE.

The President said it was gratifying to be able to open the 1934/1935 Session by presenting the Students' Medal and Prize for the year. Having been a member of the Awards Committee for more than ten years and Chairman of that Committee for some time, he would testify to the high standard of the papers which were submitted by the Students. When the Redwood Medal was awarded to the Author of the best paper or papers published in the Journal of the Institution during two consecutive Sessions, it was decided on several occasions that no paper was of a sufficiently high standard to merit the award. It was therefore noteworthy that on no single occasion had the Awards Committee considered that, of the papers submitted by Students, none was of a sufficiently high standard to merit the award of the Students' Medal and Prize. No Students' papers were submitted in 1927, but with the exception of that year the Medal and Prize had been awarded annually, while in each of the three years 1926, 1928 and 1930 an additional special prize had been awarded for a second

paper of outstanding merit. This year the following papers had been submitted by Students :—

"Some Viscometric Measurements of Clay Suspensions." By G. D. Hobson, of the Royal School of Mines.

"The Transformation of Organic Matter to Petroleum." By W. J. Gillingham, of the Royal School of Mines.

"General Principles of Corrosion and their Application to Production Equipment." By F. R. Wellings, of Birmingham University.

"Rotary Drilling Fluid." By C. W. Woolgar, B.Sc., A.I.C., of Birmingham University.

"Methods of Computation for the design of Bubble Plate Fractionating Columns for Complex Hydrocarbon Mixtures. Recent Developments and their Correlation." By J. D. Hall, of Birmingham University.

Each paper had been submitted to a referee who was a specialist in the subject matter of the paper, and the referees' reports and the papers had then been studied by the Awards Committee. As a result, the Committee recommended, and the Council approved, that the Students' Medal and Prize be awarded to Mr. G. D. Hobson for his paper on : "Some Viscometric Measurements of Clay Suspensions." Mr. Hobson was a student of the Royal School of Mines. He became a Student Member of the Institution in 1930, and in 1931/32 was awarded an Institution Scholarship tenable at the Royal School of Mines.

The question of awarding a special prize had been considered, but it was felt that, although the remaining papers were of very considerable merit, it would be invidious to single out any one for the award of a special prize.

He had much pleasure in presenting the Students' Medal and Prize to Mr. Hobson, and hoped that his success on the present occasion would prove to be an earnest of considerable future achievement.

The presentation was then made by the President.

The following paper was then read by **Mr. A. Beeby Thompson** :—

Drilling Against High Rock Pressures with Particular Reference to Operations Conducted in the Khaur Field, Punjab.

By C. E. KEEP, M.Sc., F.G.S., M.Amer.Inst. M. & M.E. (Member), and H. L. WARD.

INTRODUCTION.

THE operations to be described were carried out in the oilfield of Khaur, in the Attock District of the Punjab, a field which has not been extensively referred to in published literature, although

it has been visited from time to time by a number of the Members of this Institution and by other scientists, and some of the problems connected with its exploitation are not unknown.

The authors' excuse for presenting this paper relies on the fact that extremely high rock pressures[1] have been encountered in the field, and a description of the methods used in drilling against three pressures may therefore be of interest.

The Khaur oilfield is situated at about latitude 33° 15′ N., longitude 72° 12′ E., occupying a fairly central position in the Potwar plateau, which covers the north-western portion of the Punjab, being bounded on the north and partly on the east by the foremost ridges of the Himalayas, and on the south and partly on the west by the famous Salt Range of the Punjab.

Geology.

The geology of the Potwar has been discussed in recent years in a number of works,[2] and it is proposed to give here only sufficient geological detail as appears to bear directly on the pressure conditions of the Khaur Field.

The Khaur-Dhulian anticlinal fold lies on the northern limb of the Soan syncline, being situated about 10 miles up the dip from the axis of the syncline, which here occupies the central tract of the Potwar.

In the vicinity of Khaur the folding is not very severe, the dip on the north flank of the fold reaching a maximum of 70°/75°, while the south flank dip does not generally exceed 45°/50°.

Northwards from Khaur, in the direction of the outer ridges of the Himalayas, the folding becomes rapidly more severe. In the north of the Potwar, the folds are sharply overturned to the south and their crests crushed out of recognition; even beds of such recent time as the Pleistocene gravel are tilted in places to the vertical. This northern area is known to the geologists working in the area as the "belt of isoclinal folding."

Southwards from Khaur the folding becomes progressively more gentle. About 20 miles up the southern limb of the Soan syncline—that is, about 30 miles from Khaur, in a direction approximately at right angles to the strike—is the very gently folded anticline, or rather terrace, of Jhatla, which is discussed in R. van V. Anderson's paper.

The Himalayan folding, which is responsible for the present structures in the Potwar, has been continued from early Eocene until post Pleistocene times, and, in the words of Sir Edwin Pascoe, "it is in fact more than probable that it is still proceeding."[3]

The strata of the Khaur dome consist of sandstones, siltstones and shales of the Murree series. Although these are of late Tertiary

age, corresponding to the Burdigalian to Helvetian stages of the Miocene, they are all highly compacted. The sandstones are strongly cemented with calcium carbonate, and are of a very low order of porosity. Samples of sandstone taken from below 4000 ft. in the Khaur Field vary in porosity only between 4 and 10 per cent. Their permeability under normal testing conditions is " nil." The opinion of all workers in the area is that the movement of fluid in the rocks is confined almost entirely to joint planes and other fissures.

Origin of Pressure.

Three alternative theories may be put forward to account for the high pressures under which the fluid is contained in the rocks of the Khaur fold: that of inherited hydrostatic head, that of dead-weight earth pressure, and, finally, that of pressure induced by compressional strains in the rocks.

Regarding the first theory, Anderson and his colleagues noted that the pressure of the waters met in the Jhatla well was too great to be ascribed to normal hydrostatic head, and the interesting suggestion was accordingly made that it was an " inherited hydrostatic pressure."[4]

It was suggested that possibly the water had become sealed in the rocks up dip near the outcrop, at a time when the Salt Range was still surmounted by the Kamlial (basal Siwalik) and overlying formations. The sealing process was considered to be due either to the cementation of the pore spaces of the rocks by calcium carbonate, or to the oxidisation of oil contained in the strata; it was assumed to have proceeded in advance of denudation, so that the adjustment of hydrostatic head, that would normally have ensued as the water-bearing rocks were eroded from the upper slopes of the Salt Range, was prevented.

At Jhatla the pressures recorded are only 300 to 500 lb./sq. in. in excess of what would be expected were they due to present hydrostatic head. At Khaur they are about 3000 lb./sq. in. in excess of such normal expectations. The theory of inherited hydrostatic pressure would only be tenable for the conditions of Khaur if it could be assumed that the Murree rocks there were some 6000 ft. below their levels of exposure within the limits of the Soan syncline at the time when the fluid was sealed in the rocks.

The second theory, of earth pressure, is suggested by the similarity between the weight of the rocks underlying Khaur and the recorded rock pressures. Core samples from the wells vary in specific gravity from 2·30 to 2·60; taking an average of 2·45, a column of rock 1 ft. in height and 1 sq. in. in section would weigh 1·06 lb. A column 5000 ft. in height would have a weight of

5300 lb./sq. in., a figure which is comparable with the pressure under which the fluid is contained in the rocks at that depth. The fact that the rock pressure does so closely approach the calculated earth pressure makes one wonder whether there may have been local conditions during fairly recent geological times such as would allow the full weight of the strata to bear directly upon the fluid contained therein. There may be more than coincidence in the similarity between the "rock pressure" and the "earth pressure."

The third theory depends on the fact that the rocks penetrated by the drill at Khaur have been subjected to very great orogenic movements, which have reached sufficient severity only a short distance from Khaur to give the intense folding of the iso-clinal belt, which have certainly proceeded up to post Pleistocene times, and which may be still going on at the present. It appears more than likely that the strains set up in the rocks comprising the Khaur fold, by these movements, have not yet been relieved. Fluid trapped in the rocks would be subjected to pressure as the strata tend to become adjusted to conditions of equilibrium, and in this way very high "rock pressure" would be developed.

Of the three theories suggested for the origin of the high-rock pressures of the Khaur Field, the authors are at present inclined to believe that the last described is most likely to afford the correct explanation. However, if evidence is forthcoming from other areas, where the effects of recent folding movements are not as pronounced as they are in the Potwar, that rock pressures of the order of 1 lb. per sq. in. per ft. depth are not so unusual as is at present believed, then it is obvious that a general case may be made out for a direct relationship between earth pressure and rock pressure. At present the recorded rock pressures of the Khaur Field are regarded as being exceptionally high, and the fact that the rocks have been subjected to movements of great severity which have continued up to an exceptionally recent date, makes it appear more than likely that there is a relationship between the folding stresses and the rock pressure.

Early History of Pressure Conditions and Drilling Methods.

Even the shallowest beds gave evidence of relatively high pressure, oil sands at 100 to 500 ft. from the surface yielding flowing production in the early stages of exploitation of the field.

Cable tool wells of 1300 to 1900 ft. in depth could not be controlled by columns of water, and the realisation gradually grew that the pressures to be dealt with considerably exceeded what would be experienced were they due to simple hydrostatic conditions. At 2800 ft., wells drilled by the rotary

system could not be controlled by mud fluid weighing 80 to 90 lb. per cu. ft. (sp. gr. 1·28 to 1·44), and one or two serious blow-outs occurred at this stage. Down to about 3200 ft. sandstone predominates greatly over shale, and the holes down to this depth did not cave at all badly after the sudden release of pressure entailed by a "blow-out." Wells could be allowed to flow with several hundred feet of hole uncased, without being "beaned" at the surface, and yet there would be very little caving. Although the pressure was great, it did not afford a serious hindrance to the development of the field.

One well, 2800 ft. in depth, blew out before the water string had been set; the conductor string gave way and the well flowed wild. Some months later, after the initial violence had died down, work was resumed. It was then found that the walls had stood up, and the hole remained open to bottom. The well was accordingly brought under control and cased without difficulty.

Below about 3200 ft. the predominant formation is shale, and where much of this is exposed any sudden release of pressure caused caving to ensue, frequently to a dangerous extent.

There was a marked increase in rock pressure below the 3500 ft. level, and it became necessary to equip the walls with master valves, blow-out preventers and mud discharge "Christmas trees." In those cases where casing had been cemented directly above the high pressure sand, and little or no shale was exposed, it was a practical policy to take production without withdrawing the drill pipe from the hole. The pipe was raised a few stands from bottom, to bring the bit well up into the casing, and the well was allowed to flow either through the drill pipe or through the annulus between drill pipe and casing, back pressure being applied through beans on the flow lines, in order to combat the caving tendency of the exposed formation. When high pressures were encountered unexpectedly, often with several hundred feet of shale exposed, attempts to raise the drill pipe into the water string were foiled by the caving of the walls of the hole. Attempts to take production with the drill pipe in the hole generally resulted in sufficient loss of pressure to allow caving to commence. The drill pipe became "frozen," and a difficult fishing job ensued.

The mud fluid used at Khaur is made from a shale containing over 10 per cent. of ferric oxide,[5] and has naturally a high specific gravity in relation to its viscosity. Mud weighing 95 lb. per cu. ft. (sp. gr. 1·52) can be used quite satisfactorily in the wells for drilling purposes, but this did not prove capable of controlling the pressures encountered. One well in which water had been struck at 4400 ft. was filled with 95 lb./cu. ft. mud to the surface, and then closed in at the well head; pressure built up to 900 lb./sq. in.

in fifteen minutes and was still rising when the valve was opened in order to prevent damage to the casing.

Use of Barytes Muds.

Barytes was then turned to as a possible means of overcoming the difficulty. Fluids of relatively high clay content and weighted with barytes to 120 to 130 lb. per cu. ft. would not control the pressures, and gradually more barytes and less clay was used until finally muds weighing as much as 150/160 lb. per cu. ft. were tried.

Mud fluids of such weights are almost pure barytes—water mixtures—and are deficient in certain desirable qualities as drilling muds, but they are by no means devoid of colloided matter. The upper dimensional limit of colloidal suspensoid particles is 0·003 to 0·005 mm., and as 95 to 99 per cent. of the barytes is capable of passing a 300 mesh I.M.M. sieve, having an aperture width of 0·042 mm., much of the finer particles must come within the colloidal limit.

As relatively light muds of low viscosity proved incapable of overcoming the rock pressure, it was necessary to regard high specific gravity as the most desirable property, and muds approaching the "maximum pumpable weight" were used.

In some instances these heavy barytes muds did prove capable of controlling high pressures. In one case, a well 4300 ft. deep that had previously blown out, and become plugged by cavings, was satisfactorily repaired, cased and brought on to production with the greatest of ease, the barytes mud completely masking the presence of oil and gas until the mud was thinned down, when flowing commenced.

Such cases proved few and far between ; in the majority barytes muds of the maximum weight proved incapable of controlling the wells. A mud weighing 144 lb./cu. ft. exerts a pressure of 1 lb. per sq. in. per foot length of a column, and it became apparent that the rock pressures being dealt with were of the order of 1 lb. per sq. in. per foot depth.

One great difficulty occurred in the use of barytes muds at Khaur. The brines encountered in the field are of very high salinity—up to 18 per cent. chlorides as NaCl—and contain a percentage of high valency metal radicles. The water therefore has a coagulating effect on the colloidal particles, and tends to break down the suspension. When a water was met under sufficient pressure to overcome the pressure exerted by the barytes mud, it would flow from the formation into the hole and mingle with the mud fluid ; the mud would tend to coagulate and settle at the bottom of the hole and around the drill pipe. As a result, whenever the rotation was stopped, even for a few minutes (while making

a new connection, for example), the precipitated mud and barytes would tend to freeze the drill pipe.

Treating the mud with the usual inorganic electrolytes (such as sodium silicate, soda ash, sodium tannate, lime, the salts of weak acids and strong bases, and the salts of strong acids and weak bases) failed to reduce materially the precipitating effect of brine contamination. Experimental work still continues, however, with some promise of success.

In consequence of the action of the brines on heavy muds, attention became diverted to the possibilities of pressure-drilling methods, in which a considerably lighter mud could be used and the balance of the pressure held by means of a form of stuffing box at the well head.

Selection of Bit for Pressure Drilling at Khaur.

At depths of 3500 to 5000 ft. in the Khaur Field, fishtail bits average only 5 to 10 ft. before becoming dulled. Under such conditions pressure drilling would not be a practical policy, as an immense amount of time would be lost in snubbing, and the chances of accidental loss of pressure would be very great, in view of the frequency of bit-changing operations.

Most of the special types of bit tested showed little improvement over fishtails, and it was not until the autumn of 1931 that a bit was found capable of making much greater footage than fishtails. This was the Zublin bit. An average of 50 ft. per round trip can be made with this bit in the deep formations at Khaur, and it is primarily due to the advent of the Zublin that pressure-drilling methods have proved capable of application to Khaur conditions.

The superior footage of the Zublin bit is apparently due to the fact that if does not wobble about and cut a greatly oversize hole, as the fishtail undoubtedly did. It has been noticed at Khaur that much smaller amounts of cement are required to fill up the annular space behind casing in a Zublin drilled hole than in one drilled by fishtail bits ; this is direct proof that the Zublin does not cut out cavities in the walls of the hole to the same extent as the fishtail.

Early Application of Pressure Drilling at Khaur.

At first, early in 1932 and about six months after the introduction of the Zublin bit to Khaur, pressure drilling was used only for the " drilling-in " of wells believed to be close to productive horizons. Equipment was not installed for snubbing the drill pipe into and out of the hole as only one bit was required to drill the necessary

distance ahead, but a chamber was provided for the bit and drill collar at the top of the casing, so that it would be possible to install, and use, snubbing equipment in case of necessity.

A number of wells have been completed at Khaur under conditions of "pressure maintenance" in this manner. The drilling string consists of 5-in. O.D. "Hydril," or $3\frac{1}{2}$-in. or $2\frac{7}{8}$-in. O.D. Sullivan, flush-joint drill pipe, carrying one or more back-pressure valves, and fitted with a $7\frac{5}{8}$, $5\frac{5}{8}$ or $3\frac{7}{8}$-in. Zublin bit for drilling inside $8\frac{5}{8}$, $6\frac{5}{8}$ or $4\frac{3}{4}$-in. casing respectively. After the bit has been run to bottom, the stuffing box is packed. The hole is filled with fresh mud, and the drilling equipment is then tested by pump pressure, in preparation for drilling into the pressure zone. A pressure of 2000 to 2500 lb. per sq. in. is first applied by pumping down the drill pipe, with the mud discharge lines closed, and if this test is passed satisfactorily, the back-pressure valves are then tested by releasing the pressure on the mud pumps and drill pipe; there should be a slight drop in pressure on the stuffing box as the back-pressure valve closes and thereafter no further loss of pressure. Drilling then proceeds, with the circulating fluid passing out through beaned discharge lines at the relatively low pressure of about 500 lb./sq. in. As soon as gas is struck the control pressure is increased, by diverting the mud stream through smaller beans, until a condition of balance is obtained, the well neither making nor taking fluid, and the level in the slush pit remaining constant. On reaching the predetermined completion depth, drilling is stopped and the bit raised up a few stands, the pumps running slowly meantime to keep the full pressure on the well. Thereafter the well can be brought on to production, through the annular space between the drill pipe and casing, by opening one or more bean lines and shutting down the pumps.

When a well is completed under conditions of pressure maintenance, it is always a difficult problem to decide at what rate production may be withdrawn. Gradual loss of pressure must accompany the removal of fluid, and only local experience can guide in deciding what rate of pressure decline may be allowed without serious caving occurring.

As an illustration of the pressures that require to be dealt with at Khaur, it may be mentioned that on one occasion a well suddenly plugged the bean lines, just at the time when it was being allowed to come on to production, and in a few minutes had built up a pressure of 2750 lb./sq. in. on the well head. The pressure was still rising when one of the lines was unplugged, and it is probable that a disastrous blow-out was narrowly averted, as the casing consisted of a string of Grade C. pipe only lightly cemented.

Completion of Wells by Wash-Pipe Method.

After several wells had been completed by the use of flush-joint drill pipe, it occasionally happened that the high-pressure zone was not met where anticipated, and deeper drilling was necessary. Several thick beds of shale would be exposed below the shoe of the water string, and unless they could be cased off before the well was allowed to commence flowing, caving would occur to a serious extent. Perforated strings of casing cannot be run into a well while the pressure is being controlled through well-head stuffing boxes, as the fluid would be free to escape from the well through the perforations of the first few joints. It was necessary to provide some means whereby the drilling string, or a part thereof, could be left in the hole to serve as casing and prevent the formation caving.

Accordingly, Mr. Ward devised a method whereby a perforated casing liner can be used as part of the drilling string and can later be " backed off " and left in the well to keep the hole open. In order that the mud flush may be directed down to the eyes of the bit during the process of drilling, and not be able to escape through the perforations of the casing section, a wash pipe of $1\frac{1}{4}$-in. tubing is run throughout the length of the casing, firmly sealed off to the drill pipe at the top and to the drill collar at the bottom. The upper seal is provided for by connecting the wash pipe into the upper half of the safety joint which connects the casing to the drill pipe, and the lower seal is effected by furnishing the top of the drill collar with a conical recess into which a special tapered coupling run on the bottom of the wash pipe may sit.

As an illustration of the method used, let us assume that a well cemented in $8\frac{5}{8}$-in. casing at 4550 ft. has been deepened to 4600 ft., under pressure control arrangements as previously described, but has failed to pick up the expected high pressure production, and is to be drilled ahead prospecting for another possible productive sand. In such a case, the drilling string would be composed of the following items: (1) A $7\frac{5}{8}$-in. Zublin bit; (2) a short drill collar, carrying near its base a back-pressure valve, and shaped at the top so as to form a tapered and ground seat; (3) about 200 ft. of $6\frac{5}{8}$-in. casing perforated suitably near the base; (4) a safety joint, from the upper half of which would be suspended about 200 ft. of $1\frac{1}{4}$-in. tubing; (5) a back-pressure valve; and (6) $3\frac{1}{2}$ or 5-in. flush-joint drill pipe extending to the surface. The bit, drill collar, casing, and the lower half of the safety joint are connected together and run in the usual manner; then the $1\frac{1}{4}$-in. wash pipe, fitted with a tapered and ground coupling, is run inside the $6\frac{5}{8}$-in. casing until the coupling seats in the top of the drill collar. The uppermost joint of the tubing is now

painted with a mark level with the bottom of the safety joint. The tubing is then removed and is cut off at a point above the paint mark which will allow it to be screwed home into the male end of the safety joint. When the tubing is replaced, then the paint mark is again exactly at the bottom of the safety joint and lowered so that the bottom seats in the conical recess in the drill collar again. This leaves the upper half of the safety joint about 1 in. above the lower half. The two are forced together and screwed up, thereby putting the tubing in compression and forcing the bottom coupling well home into the seat in the drill collar. The drilling string is then completed by addition of the back-pressure valve and the flush-joint drill pipe. Drilling proceeds, the mud flesh passing down from the drill pipe and through the $1\frac{1}{4}$-in. tubing to the eyes of the bit. When it is required to stop the well and take production, the drill pipe is rotated in a counter-clockwise direction to open the safety joint, and detach the casing liner from the drilling string. The flush-joint drill pipe may then be pulled up several hundred feet, carrying with it the $1\frac{1}{4}$-in. washpipe, and flowing production taken through the perforations in the liner and thence between the drill pipe and the casing.

"Vernier" type weight indicators have been found of great value in indicating whether or not the liners have been safely backed off, particularly when only a few joints are in use.

The wash-pipe-liner method of drilling into zones of high pressure has been of great value at Khaur. It affords a ready method of drilling and casing wells in one operation, without release of pressure. Flowing production can be taken from the well until the pressure is relieved to such an extent as to allow of the casing-head being opened. In one case a liner of $4\frac{3}{4}$-in. casing nearly 900 ft. in length was used in a well lined with $6\frac{5}{8}$-in. casing, and very fair footage was obtained.

There are, of course, obvious objectionable features to the method. For example, it is not possible to make a round trip with the drilling string under pressure control ; once high pressure conditions have been struck the only further progress that can be made depends on the condition of the bit. Again, it would not be possible to pull the $1\frac{1}{4}$-in. tubing from the hole, under pressure control, without a complicated system of stuffing boxes. A modification of the drill-pipe back-pressure valve, so as to allow of its being opened or closed at will, might effect a great improvement in the flowing efficiency of the well during the production stage ; the flow could be taken through the $1\frac{1}{4}$-in. tubing, and the drill pipe, instead of through the annular space between drill pipe and casing.

Control Pressures Necessary at Khaur.

When drilling under pressure at Khaur, the control pressure is increased to the extent necessary to prevent fluid entering the well from the formation. Wells at depths of 4800 to 5300 ft. usually require a control pressure of 2000 to 2300 lb. per sq. in., imposed on a column of mud fluid weighing 85 to 95 lb. per cu. ft., in order that this condition may be satisfied.

Calculated Rock Pressures.

Abraham and Singleton have shown that closed-in well-head pressure may considerably exceed the difference between the rock pressure and the pressure exerted by the mud column, owing to the fact that bubbles of gas in the mud will tend to rise to the top of the well. Usually fluid can only be driven back into the formation with difficulty, if at all, so that the gas bubbles have little opportunity for expansion, and remain under relatively high pressure. That this is so has been clearly proved.[6]

It is important, therefore, to establish the fact that the calculated rock pressures of Khaur are based not on closed-in well-head pressures, but upon the control pressure which it is necessary to hold on the circulating fluid in order to prevent ingress of fluid from the formation. Under these circumstances the sum of control pressure and mud-column pressure is clearly equal to the rock pressure.

There have been many instances in the field of control pressure "plus" mud-column pressure equalling or exceeding 5000 lb. per sq. in.

Pressure Drilling of Deep Test Well.

In the development of the Field, high-pressure oil and gas sands tapped by wells drilled under conditions of pressure maintenance, in the manner already described, could be produced, by natural flow, under controlled back pressure, until the pressure declined. A high-pressure water sand was, however, met in a number of wells, at depths corresponding to a crestal level of 5100 ft. below the surface. This sand generally carried a large volume of water except in the western portion of the field, where it had yielded little water; two wells deepened through the sand in this part of the field had encountered a second water-bearing sand, termed the 5300 ft. sand. Before exploring the underlying rocks it was therefore necessary to drill through the 5100 and 5300 ft. sands. Two alternatives presented themselves: firstly, to drill through the sands against the full rock pressure, or, secondly, to drill into the water sands at selected points (old small diameter wells) and allow the water to flow, until such time as the pressure would become dissipated to a more easily controlled level.

A certain amount of water had been produced from two or three wells in the 5100 ft. sand, with the object of relieving the pressure, when it was decided to proceed with the deep testing of the field. It is with the drilling of the selected well through the 5100 and 5300 ft. horizons that this paper now deals.

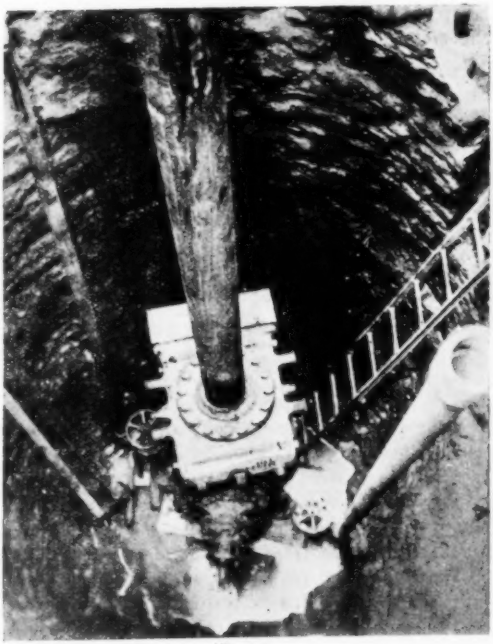

FIG. 1.

Cellar of Deep Test Well with drilling riser in course of construction. One of the mud lines rising from the mud cross may be seen on the right of picture. The mud cross is submerged in water, but above it may be seen the bottom control gate (which was fitted with blind rams), the master valve, the second control gate (fitted with drill pipe rams) and 8⅝-in. chamber for drill collar and bit.

The well had been cemented directly over the 5100 ft. sand in 8⅝-in. 38 lb./ft. A.P.I. casing at 5206 ft. Although the casing was only Grade C. material the cement job had been a heavy one, 850 cwt. of cement being used and cement returns being obtained at the surface. It was, therefore, considered safe to use pressure drilling methods inside the string, and this in fact proved to be so.

The hole was carried from 5214 ft. to 5693 ft. with 7⅝-in. Zublin bits, and a string of 7-in. O.D. Hydril flush-joint casing then cemented with the shoe at 5685 ft. It is this stage of the progress of the well that is now discussed.

Well-head Control Connections.—The cellar was deepened to 34 ft.—measured from the base of the derrick floor sills—and the drilling riser built up, in the following order, reading upwards from the floor of the cellar :—

(*a*) A Kerotest mud cross.
(*b*) A Shaffer control gate fitted with blind rams.
(*c*) A Kerotest master valve.
(*d*) A Shaffer control gate fitted with 5-in. drill pipe rams.
(*e*) A 15-ft. length of 8⅝-in. casing to serve as "gun barrel," or chamber for drill collar and bit.
(*f*) A Shaffer control gate fitted with 5-in. drill pipe rams.
(*g*) A Kerotest mud cross.
(*h*) A Doheny Stone Hydril 5-in. Drilling Head, complete with hydraulic bag packer fitted below the drilling packer.[7]

Both the Kerotest crosses were connected to the mud outlet lines and also to the mud pump discharge manifold, so that either could be used for outgoing or for ingoing mud.

The outgoing mud lines passed from the crosses to special traps, installed for the purpose of removing rock fragments, and thence to a battery of "beans" of both the adjustable and the drilled plug type. The traps were constructed of vertical 8⅝-in. pipes in which were suspended perforated 3-in. pipes, the mud entering the annulus between the pipes and passing out through the 3-in. pipe. In this way the coarse fragments of formation cuttings were filtered out from the mud before it passed to the beans ; plugging of the beans was prevented, and formation samples were recovered periodically by back flushing the traps.

Mud Fluid and Pumps.—Before deepening commenced it was decided to make every attempt to control the well with ordinary, unweighted, shale mud, in order to avoid the dangers attending the contamination of heavy barytes muds by salt water. As it proved possible to control the rock pressure with ordinary mud, using a high well-head pressure, it was not necessary to use laden mud. The well was therefore drilled with shale mud weighing about 90 lb. per cu. ft., throughout the interval 5214 to 5693 ft.

The mud pumps used were of the conventional steam-driven type, 14-in. steam cylinder, 7¼-in. fluid cylinder and 14-in. stroke, and were used compounded together in series, the first stage, or pick-up, pump being fitted with a low-pressure mud end and the others with 3000 lb./sq. in. fluid ends. At first, drilling at

5214 to 5478 ft., a bean pressure of 1800 lb./sq. in. was required to control the well. To obtain this, three pumps were compounded in series, the first fitted with 6-in. liners in the mud cylinders, the second and third with 5-in. dia. liners. Steam was furnished at 200 lb./sq. in. at the boilers, and the pump discharge pressure under these conditions was about 2250 lb./sq. in. Later on, at 5478 to 5693 ft. the control pressure had to be maintained at 2000 lb./sq. in., and four pumps were then compounded together, equipped with 6-in. liners, and giving a pump pressure of 2700 lb./sq. in. At all times there was one spare pump to serve as a standby, there being a total of four pumps at first and later five pumps in the battery.

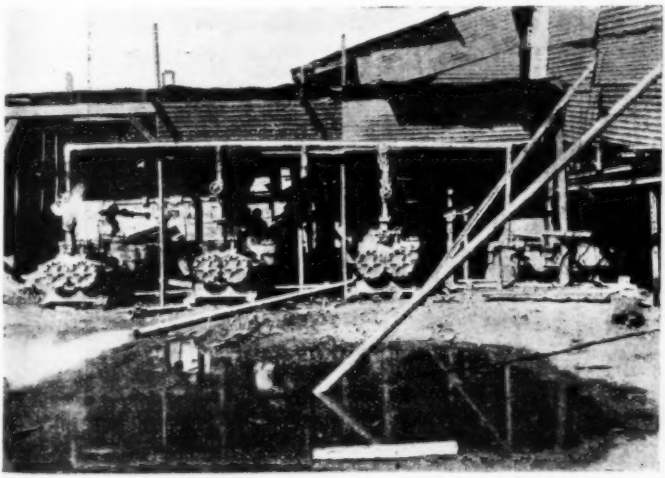

FIG. 2.

A view of some of the pumps used for the Deep Test Well. Three of the 14-in. × 7¼-in. × 14-in. mud pumps and the 20-in. × 3½-in. × 12-in. high pressure pump are shown.

The steam supply to the mud pumps could be controlled by a valve on the derrick floor close to the hand of the driller.

A high-pressure steam-driven water pump — 20-in. steam cylinder, 3½-in. water cylinder, 12-in. stroke—was also connected up, being used for delivering water to the hydraulic bag packer on the Doheny Stone head, or to the mud pump manifold and drill pipe. In connection with the latter service, it will be realised that

when making a round trip with drill pipe under pressure drilling conditions, the string is full of fluid and cannot be pulled "dry." To overcome the disadvantages of having mud ejected from the drill pipe as each stand was disconnected, a measured volume of water was pumped into the drill pipe periodically to displace the mud from a certain number of stands. In this way the derrick floor was kept clean and the top packing rubbers did not get covered with mud when the pipe was being pulled ; the drilling riser and cellar were also kept free from mud.

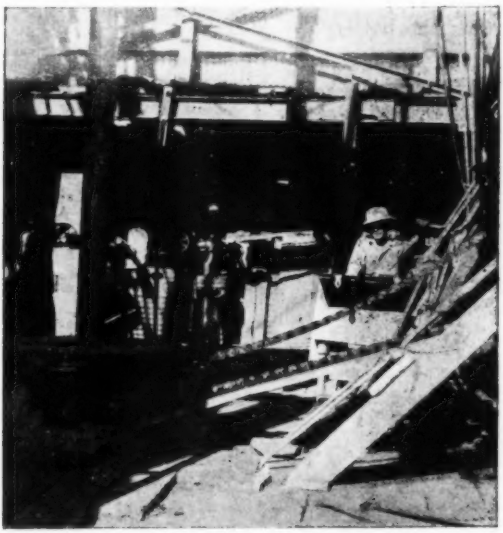

FIG. 3.

A view of the Deep Test Well, in process of drilling. The special 8¾-in. pipe used as a hollow Kelly, inside which the 5-in. drill pipe was suspended, is in position fitted into the table.

Between the driller and the table may be seen the top of one of traps used for removing coarse fragments from the mud fluid.

Connections from Pumps to Drill Pipe.—The rotary hose used for connection from the pump manifold to the swivel was a Champion all-steel hose tested to 5000 lb./sq. in. The swivel was of Oil Well Supply Co. manufacture, 6-in. size Imperial No. 150 type. Both swivel and hose stood up excellently to the heavy duty demanded of them.

Drill Pipe and Method of Drive.—The drill pipe used for the deepening of the well consisted of 5-in. O.D. Hydril flush-joint drill pipe Grade D. 20·5 lb./ft., supplied in 30-ft. lengths with box connections at each end and equipped with a tool joint per length. The pipe was handled in stands of three joints, a uniform length of 90 ft. per stand. As the standard type of rotary table was in use it was necessary to devise a satisfactory method of rotating the drill pipe. This problem was solved by taking a length of $8\frac{5}{8}$-in.

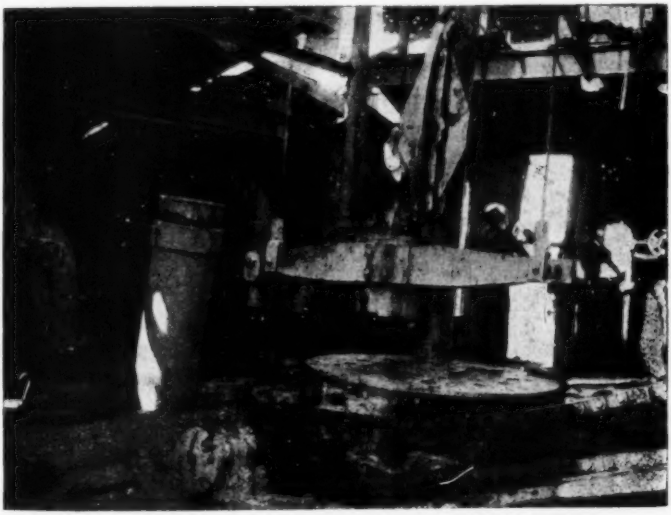

FIG. 4.

The Deep Test Well, showing the left-hand side of the rig. The auxiliary draw-works, used for snubbing, is on the left of the picture, and in front of this is the 20-in. casing protruding from the Kelly rat-hole.
Above the table is the drill pipe snubbing bar.

casing 35 ft. long and welding to it two special bushings, the lower bushing fitting into the rotary table in place of the usual Kelly bushing, and the upper bushing made to take a standard 4-in. square Kelly as a sliding fit ; with this pipe set in the rotary table the drive was transmitted from the table, through the length of the $8\frac{5}{8}$-in. pipe, to the upper bushing. The flush-joint drill pipe was screwed to a 4-in. square Kelly and this lowered into the upper bushing of the $8\frac{5}{8}$-in. pipe, so that the string could be rotated in the normal manner, but with the Kelly bushing some 35 ft. above the

level of the table. As the square Kelly was 30 ft. long it could be drilled down the full length inside the $8\frac{5}{8}$-in. pipe without interfering in any way with the installation of the drilling riser, which was of course only suitable for the 5-in. flush-joint pipe, and was installed a few feet below the derrick floor. After 30-ft. of hole had been made, another single joint of drill pipe would be added to the string and drilling resumed.

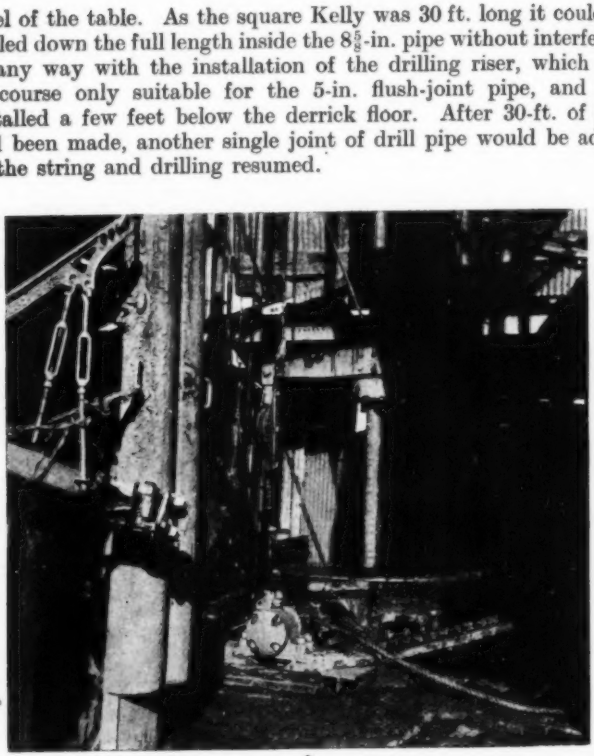

FIG. 5.

Snubbing drill pipe at the Deep Test Well.
Arrangement of snubbing bar and wire-line tackle may be seen. The drawworks on the right exerts the upward pull, while that on the left (not shown in photo) acts through the snubbing equipment to exert a downward pull on the drill pipe.

Kelly Rat-hole.—The rat-hole used for setting the Kelly back out of the way, when not in use for drilling operations, had to be specially arranged to take the $8\frac{5}{8}$-in. pipe. It was drilled to a depth of 50 ft. and cased with 20-in. O.D. drive pipe, into which a platform of steel bars was welded half way down. When the pipe was pulled from the well, the whole Kelly assembly, including the $8\frac{5}{8}$-in. pipe, the square Kelly, and, if necessary, a single joint of the 5-in. drill pipe, could be lowered into the rat-hole. Not only

did this leave the derrick clear of a considerable amount of impedimenta, but it also allowed easy inspection of the top Kelly joint and the swivel.

Snubbing of Drill Pipe.—For snubbing the drill pipe into or out of the hole a snubbing bar and a stationary hold down were manufactured at the field. The equipment was operated by wire lines passing over single-sheave blocks suspended from either end of the snubbing bar, and double-sheave blocks bolted to the stationary hold down, so that a three-line pull could be given. A second draw-works, of light type, was installed on the pump side of the derrick floor for operating the snubbing bar ; this draw-works served to pull the snubbing bar downwards, while the main draw works was employed to keep a tight hold on the drill pipe and would have prevented it falling back down the hole had there been an accidental release of pressure from the well. The snubbing bar itself was suspended in the rig from wire lines passing over a pulley carried by the sand line, and was raised or lowered by the operation of the sand reel whenever a new hold had to be taken. It will be noted that three hoists were in use—namely, the main draw-works, used for feeding the bit in the process of drilling and for exerting an upward pull on the drill pipe during round trips, the auxiliary draw-works, used for pulling downwards on the snubbing bar during snubbing operations, and the sand reel, used for raising or lowering the snubbing bar when it was required to take a fresh hold of the pipe.

Using drill pipe of 5-in. diam. and weighing 20·5 lb./ft., approximately 1 ft. of pipe has to be snubbed for each lb. per sq. in. pressure held on the casing head. Accordingly, under the pressure conditions ruling, it was necessary to snub two to three thousand feet of the drill pipe in and out of the hole at all round trips. Even in such an extreme case as this, the snubbing effort that is required is not great, and it is possible to handle the pipe rapidly with safety. The minimum ultimate strength of 1-in. diam. Grade J. 6/19 wire line under A.P.I. rating is 69,000 lb. The maximum load was only about 50,000 lb. and six lines were used in snubbing—three on each side of the bar—so that a safety factor of 8 was allowed. When snubbing against the maximum load three hitches were taken for each stand of drill pipe, that is the snubbing bar was allowed to travel a distance of 30 ft. before a new hold was taken ; when the load was lighter a stand of pipe was snubbed in two hitches, the bar being allowed to travel 45 ft. before a new hold was taken.

During the process of snubbing the main draw-works pulls upwards on the drill pipe while the auxiliary hoist acts through the snubbing bar to give a downward pull. No difficulty was

experienced at the transition, or "floating," stage, when the amount of pipe in the hole is just about sufficient to balance the pressure, as the draw-works pull against one another. The snubbing bar holds more than sufficient downward pull on the drill pipe to overcome the tendency of the well to blow the pipe out of the hole, and the main draw-works and hoisting tackle have to be brought into use to raise or lower the pipe as required. When the main blocks are disconnected from the drill pipe, as the stands are

FIG. 6.

Another view of the Deep Test Well with snubbing equipment in use. A stand of drill pipe has just been unscrewed. On the extreme left of the picture is the auxiliary draw-works, and to the right of this (above the coolies' heads) may be seen part of the swivel and Kelly, which have been set back in the Kelly rat-hole.

being removed from or added to the string, the usual table slips serve to prevent the drill pipe from falling, and the stationary hold-down prevents it being blown out of the hole.

While running or pulling the drill pipe, it was of course necessary to offset the increase or decrease in volume occupied by the drill pipe in the hole. When pipe was being run, mud had to be bled off from the casing head to maintain the pressure at a constant; when pipe was being pulled, mud had to be forced into the well by the pumps for the same purpose.

Wear and Tear on Control Equipment and Need for Rapid-Closing Valves.—When pressure-drilling operations are in hand it is imperative that the rig and table be correctly aligned, otherwise the well-head fittings become subject to rapid wear. At the well now under reference difficulty was experienced owing to a slight error in alignment ; a leak developed at the base of the chamber, and it was found that the oscillations of the drilling riser had caused severe wear in the threads of the casing nipple.

Gas working on packing rubber soon renders it porous and brittle, and no longer effective. Every endeavour was made to prevent gas entering the hole from the formation, but there was sufficient present in the mud to affect the rubbers, and these required changing from time to time. Generally it appeared that the heavier and more solid type of packing rubber stood best to the somewhat gassy conditions.

It was obviously necessary to be in a position to close the well in very rapidly, in case of signs of any leak in the control equipment. For this purpose mechanical means were rigged up for operating the more important well-head valves.

A countershaft was set up below the derrick floor, fitted at one end with a cat-head and at the other with two sprocket wheels. The shaft was driven from the cat-head by means of a rope which could be thrown on to the cat-head of the auxiliary draw-works at any moment, and the sprocket wheels could be connected by chain to similar wheels fitted to the spindles of the master valve and one of the drill-pipe ram gates.

Normally, when the drill pipe was in the hole, and extending below the master valve, the chain from the countershaft sprocket was connected to the drill-pipe ram gate. This gate could then be closed at a moment's notice by spinning the rope on the cat-head of the auxiliary draw-works. Once the bit had been pulled up into the chamber, the master valve could be similarly operated by chain drive from the countershaft.

Subsequently arrangements have been made for the operation of the drill-pipe ram gate by means of an electric motor, controlled by a switch close to the hand of the driller.

Indicating and Recording Gauges.—Mud-weight scales were set up in the slush pit and in the mud ditch to indicate and record the weight of the mud fluid at the pump suction and at the outlet from the well.

The pump discharge pressure and the control pressure held on the mud outlet lines from the well were indicated and recorded by means of the usual Martin Decker equipment, embodying special diaphragms and vibration dampers to prevent damage to the gauges either by intrusion of mud or by the frequency of the

pulsations. A comparison of the daily charts obtained from these mud-pressure gauges was of immense value in checking up the operations at the well over a period.

A panel was erected in front of the main draw-works, and facing the driller, to carry all the indicating gauges to which his attention was necessary, these comprising the weight indicator and vernier gauges, the two mud-pressure gauges, a gauge showing the steam pressure on the engine manifold, and a gauge showing the available steam pressure at the rig.

FIG. 7.

A view of the mud ditch and slush pit of the Deep Test Well. Mud weighing scales in use. Slush pit constructed of M. S. plates and projecting above ground level to minimise suction load on pump.

Pressure Conditions met in Drilling.—As has been previously noted, the 8⅝-in. casing had been cemented directly over the 5100 ft. sand, at a depth of 5206 ft. After the cement left inside the hole had been cleaned out the well commenced to show water and it became necessary to increase the control pressure gradually until the flow was killed. At 5215 ft. mud fluid weighing 88 lb./cu. ft. was being circulated against a pressure on the beans of 2000 lb./sq. in.; it appeared that there was no gain in level in the

slush pit and that the rock pressure was approximately balanced. The rig had to be shut down a short while for repairs and the closed-in pressure then rose slowly to 2150 lb., and stayed at that level for half an hour until work was recommenced. It is probable that this rise in well-head pressure, from 2000 to 2150 lb./sq. in., was due to the effect of gas bubbles rising through the mud, although when circulation was resumed there was no apparent evolution of gas from the well-head, or any decrease in the mud weight.

As drilling proceeded, it was noted that the well alternately yielded water from the formation, or extracted water from the mud fluid, dependent on whether the control pressure was allowed to fall or rise respectively. If the pressure fell, water would enter from the formation and dilute the mud, but what was much more unusual was the fact that if the bean pressure were increased appreciably the mud returns would shrink in volume and show increased weight and viscosity; there was no doubt that the free water was being squeezed out of the mud fluid and filtered into the formation. If this process were allowed to go on unchecked, the mud would become more and more viscous until the limit of "pumpability" was approached; if the bean pressure were reduced water would pass back from the formation and the mud would "thin up."

On one occasion, after a round trip at 5447 ft., new mud weighing 94 lb./cu. ft. was pumped into the well against a bean pressure of 2100 lb./sq. in. The weight of the return mud rose gradually from 94 to 96 and finally to 98 lb. per cu. ft. Lowering of the bean pressure and the addition of lighter mud allowed the previous conditions of balance to be re-obtained.

From 5215 to 5478 ft., the control pressure had to be kept at 1800 lb./sq. in., using 90 lb./cu. ft. mud fluid, in order to prevent the well yielding water. The rock pressure at 5215 ft. may therefore be calculated as 5060 lb./sq. in.

Later this formation apparently became sealed off, as after the 5300 ft. sand had been struck, at 5478 ft., it became necessary to use a still higher control pressure, and this proved possible without loss of water from the mud. From 5478 to 5693 ft. the control pressure had to be maintained at 2000 lb./sq. in., with 90 lb./cu. ft. mud, to prevent a gain in volume of the circulating fluid. The rock pressure at 5478 ft. appears therefore to be about 5420 lb./sq. in.

Running and Cementing of Casing under Pressure.—On reaching a depth of 5693 ft. it was decided to cement casing in order to exclude the 5100 and 5300 ft. sands. For this purpose a string of 7-in. O.D. flush-joint Hydril flush-joint seamless casing, 30 lb./ft., Grade D., had been obtained.

A Seamark blow-out preventer,[8] comprising two single static heads, suitable for $8\frac{5}{8}$-in. casing, and complete with hydraulic intensifier was available at the field. This preventer had previously been employed at one well, where a string of $6\frac{5}{8}$-in. collared casing was successfully run and cemented inside $8\frac{5}{8}$-in., at a depth of 4280 ft. against a control pressure of 1100 lb./sq. in.

The top Shaffer gate of the drilling riser was fitted with rams to close against the 7-in. casing, and the Doheny Stone Drilling Head was replaced by the Seamark blow-out preventer fitted with 7-in. packers.

The snubbing equipment for running the casing was somewhat heavier than that used for the drill pipe, but was operated in a similar manner, by wire lines leading from the auxiliary draw-works. The running of the casing was done under a bean pressure of 2000 to 2400 lb./sq. in., but proceeded as smoothly as an ordinary casing job. It was not until a depth of over 3500 ft. was reached that the casing in the hole balanced the well pressure. The snubbing equipment had to be kept in use thereafter to force the pipe through the blow-out preventer, and it was only after 4190 ft. had been run that snubbing was no longer necessary.

The casing stopped at one or two points after the shoe had reached uncased hole, but by circulating for a few minutes and then shutting the pumps off, it was possible to carry it safely past these levels. It is to be borne in mind that the effective weight of the pipe was only that of the position below 4190 ft. Obstructions that would scarcely be noticed in the running of casing in the normal manner might be sufficient to arrest the progress of the pipe run against high pressure. As it was, the obstructions were presumably due to a filter pack of mud having been built up against the walls of the hole during drilling operations. The casing was finally carried to a point 8 ft. off bottom and there cemented.

Two Baker float valves were in use, one in the first coupling and one in the cement shoe; these did not leak throughout the job, and maintained the pressure seal inside the casing as completely as the Seamark blow-out preventer did outside the casing.

238 sacks of cement (112 lb. each) were used in the cementation. While pumping the cement the bean pressure was gradually reduced to 1500 lb./sq. in. in order to increase the pumping speed and place the cement in position rapidly. The pump pressure necessary to obtain this pressure at the beans amounted to 2300 to 2500 lb./sq. in.; once the cement had been placed, the pumps were put on to the annular space between the $8\frac{5}{8}$-in. and the 7-in. casings and a pressure of 2250 lb. built up thereon. All valves were then closed and the cement allowed to set, 95 mins. having

elapsed from the initial wetting of the cement to the completion of the cementation.

After standing 14 days, the 7-in. casing was opened at the head and the cement job tested and found to be successful, the water being sealed off both from the hole and from the annular space between strings. On reaching the depth of 5715 ft. the well was bailed down to 2000 ft. and showed only a small gain in fluid level, which appeared to be due to gas rather than to water. The well had been carried through the high pressure waters and these were now successfully excluded from the hole.

ACKNOWLEDGMENTS.

In conclusion, the authors wish to express their thanks and appreciation to Messrs. Steel Bros. and Co., Ltd., and Messrs. The Attock Oil Company, Ltd., for their very kind permission to publish this paper.

REFERENCES.

[1] To avoid confusion it should be stated that the term "rock pressure" is used as implying the pressure under which fluid is confined in the rock, irrespective of the cause of the pressure.

[2] Prominent among the recent literature on the area are: E. S. Pinfold, "Notes on the Structure and Stratigraphy in the North-West Punjab," *Rec. Geol. Sur. Ind.*, 1918, **49**, 137, and "The Conditions Governing the Occurrence of Oil in the Punjab," Pres. Address, Fifth Ind. Sci. Congress, *Journ. Asiat. Soc. Beng.*, 1918, New Series, **14**, No. 6. Sir E. H. Pascoe, "Petroleum in the Punjab," *Mem. Geol. Sur. Ind.*, 1920, **40**, Pt. 3. R. van V. Anderson, "Tertiary Stratigraphy of the Northern Punjab," *Bull. Geol. Soc. Amer.*, 1927, **38**, 665.

[3] Sir E. H. Pascoe, *op. cit.*, p. 451.

[4] R. van V. Anderson, *op. cit.*, p. 708.

[5] Analysis of the shale (after air drying) by the Department of Agriculture, Punjab Government, gave the following results: SiO_2, 66·148; Al_2O_3, 12·19; Fe_2O_3, 10·75; MgO, 0·29; CaO, 7·48; K_2O, 0·945; Na_2O, 0·798; SO_3, 0·034; P_2O_5, 0·111 per cent.

[6] W. E. V. Abraham and W. Singleton, "Effect of Gas Bubbles in Circulating Fluid on Recorded Shut-in Casing Head Pressures," *Proc. World Petr. Congr.*, 1933, Vol. 1, 407.

[7] The Doheny Stone Head is of the type illustrated and described by B. J. Ellis and J. Cuthill in "Pressure Drilling," *Proc. World Petr. Congr.*, 1933, Vol. 1, p. 361.

[8] As described by B. J. Ellis and J. Cuthill in "Pressure Drilling," *Proc. World Petr. Congr.*, Vol. 1, p. 361.

DISCUSSION.

The President said there would be general agreement that they had listened to a most interesting paper on a very important subject. The Khaur field was unique in many ways and was, in the first place, noteworthy owing to the contrast which it offered between the surface and the underground conditions. With regard to the surface geological structure, the topography and the general lay-out, the field seemed to be a very simple and even

an ideal oil field, although a little investigation showed that the simple and ideal conditions did not persist very far underground, where one was soon confronted by a number of puzzling and fascinating problems. One of those was, as the authors had pointed out, that of the cause of the very high pressures encountered during drilling. Three hypotheses were advanced in the paper to account for those high pressures : (1) That the pressure was inherited hydrostatic pressure, or, he might say, fossil Murree pressure ; (2) that it was due to earth pressure ; and (3) that it was due to folding stresses. In considering those hypotheses, it seemed very significant that at Jhatla the pressures in excess of the hydrostatic head were only 300 to 500 lb. per square inch, whereas at Khaur the excess was about 3000 lb. per square inch, and it might therefore be interesting to consider why such differences in pressure existed in the two areas, which were situated on opposite sides of one and the same syncline. On the first hypothesis it would be necessary to explain why the inherited pressure had largely been dissipated at Jhatla and preserved at Khaur ; with regard to the second hypothesis, it was difficult to understand why earth pressure should have operated so much more effectively at Khaur than at Jhatla, and in regard to the third hypothesis it seemed doubtful if the difference in the folding stresses to which the two areas had been subjected would be sufficient to explain the very striking difference in the underground pressures. He would draw attention to an additional possibility. The Murree waters at Khaur were extremely saline, and as the Murrees and the younger rock groups were of fresh water origin it was clear that the saline water in the Khaur field was of pre-Murree age. No saline water was encountered while drilling through the Nimadric system at Jhatla, and therefore he would stress the possibility that intrusion of saline waters from below was an important contributory cause of the high pressures at Khaur.

The result of the existence of high pressures was that the Khaur oil field presented an object lesson in regard to the difficulties, such as high pressures, serious caving, etc., which were encountered in modern deep drilling, and it followed that the presentation of those difficulties and of the methods employed in combating them gave great value and weight to the paper.

He did not propose to comment on the technical aspects of the paper, as fortunately several experts were present who would be able to discuss such matters with authority. Nevertheless, he was sure that everyone present that evening readily and fully appreciated the formidable drilling difficulties encountered in the Khaur field and admired the courage, the patience and the ingenuity

displayed by the authors and their colleagues in overcoming those difficulties.

Mr. B. J. Ellis said that the interesting sequence which led to pressure drilling should be carefully noted—blow-outs, heavy muds, weighted muds, pure barytes muds, and then pressure control, but the latter only after a bit had been discovered which would make a fair amount of hole without pulling out. He thought it very interesting to note that the people concerned went out first to find the bit that would do the drilling, and then, when they had found it, decided that pressure drilling was possible. The paper constituted an ample answer to those who doubted the need for pressure drilling; that doubt had been expressed at previous meetings of the Institution, and a query had been raised as to when it should be adopted. It was obvious that the work at Khaur could not have been done without it, and that the time for its adoption was when other methods failed to maintain control.

Personally he had nothing but admiration for the way in which all the difficulties at Khaur had been tackled. It might interest the authors to know that some of the devices they used, or some very similar devices, had been developed in Burma, but in Burma the success which the authors achieved had not always been obtained. Traps for shale cuttings had been tried, but they did not extract the shale and the beans plugged very badly; it had not been possible to achieve satisfactory results, in one area at least, until a closed circulation system was used.

He had never before heard of four pumps being compounded in series. That was just another example of the way in which the Authors got on with their job and, when they came to a difficulty, tackled it.

It was most interesting to him to hear that the drilling was carried out with an ordinary rotary table. He had always disagreed with those who insisted that an hydraulic rotary table was essential for pressure drilling, and he was glad to have his views confirmed by the actual experience of the authors. The driving arrangement for the drill pipe described in the paper had been used on one well in Burma, the drilling being at a moderate pressure, but for some reason, probably because hydraulic tables had been provided, it had not been used again.

He was a little doubtful whether the deterioration of the rubber, particularly the hardening of the rubber, in the packers was due entirely to gas. In a well in Burma that was cemented off at the bottom and in which there was no possibility of any gas being present, some experiments had been carried out to test two or three types of rubber packers, and it was found that after the

rubber had been subjected to a high pressure it was hard and brittle. It seemed possible that the pressure itself was responsible for the hardening of the rubber, and manufacturers of rubber could do a great service to petroleum technologists by investigating the matter and seeing whether they could not make a rubber which would not harden under pressure.

The only suggestion he could put forward to assist the authors in their further operations was the use of the closed circulation system, which had been described in a paper written by Mr. Cuthill and himself for the World Petroleum Congress. The system had been in use in one well for the past six or eight months, and had proved to be an entire success. It obviated the use of beans, which, as the authors would no doubt agree, gave rise to trouble, and, instead of the need of four pumps compounded together, one pump alone could be used for circulation, as the suction pressure to that pump was very little below the discharge pressure, the difference being only 400 or 500 lb.

Mr. W. E. V. Abraham said that, as Mr. Ellis had said, pressure drilling had been forced on the Khaur field. Even if there had been no trouble with salt water the continued use of muds weighing as much as 160 lb. per cub. ft. would have introduced many difficulties. When there was added to these the coagulation of the mud due to the very saline water, many times more salty than the sea, the difficulties became insuperable and pressure drilling offered the only hope of success. At first it was used only for drilling into a known high pressure zone where oil was expected, but later Mr. Ward's ingenious device allowed it to go a step further and deal with drilling into a supposedly productive zone plus a small subsequent deepening if this became necessary. Lastly, even that was not enough; it was necessary to get far below the high pressure water zones, and a complete pressure drilling outfit had to be used.

In connection with this sequence of events no one who had been at Khaur could fail to be impressed both by the variety and the magnitude of the difficulties that had to be overcome and by the energetic way in which they had been tackled by the people on the spot.

Considering now the actual deep test, he was greatly interested in the behaviour of the mud fluid under pressure. The authors explained that for a certain zone a pressure above a certain amount caused water to be expressed from the mud into the sand, and that at pressures below that critical pressure water would come back from the sand into the well and mix with the mud again. For any one zone the difficulty could be met by arranging to apply the critical or balancing pressure at which water moved neither

into nor out of the reservoir rock, but clearly this solution could not be applied if there were several zones each demanding a different balancing pressure. The authors do not refer directly to this difficulty, but merely mention that it was found that, after they had drilled through a particular zone, that zone must eventually have become sealed, because later on they reached a zone for which the critical or balancing pressure was greater than before, and they were able to apply this greater balancing pressure without causing water to go into the higher zone. That was fortunate, and he suggested that if one were drilling through many such zones, it would be necessary to arrange for the mud to be of such a kind that when a sand was entered by the drill, and a little water was expressed from the mud into the sand, a seal was produced fairly quickly against further passage of water into the sand. The opposite effect of arranging that no water should come back from the sand into the hole when the pressure was lowered, was, of course, a much more difficult problem, and one for which, so far as he was aware, no solution was available.

He was greatly interested in the President's reference to the three theories—to which the President had added a fourth—as to the origin of the very high pressures, and would like to consider this matter not only from the point of view of the Khaur field, but from the point of view of the possible more general application of one or more of these theories. The first one, that of inherited water pressure, was no doubt properly applied by Anderson in the particular case in question, but, so far as he was aware, it could not be used to explain, in other parts of the world, a number of those high pressures which in the past we had been content to call "abnormal." The same, he believed, applied to the President's suggestion of a pressure originating from below. A third theory, that of pressure induced by compressional strains in the rocks, if it applied at all, could have, he presumed, a very general application all over the world. An interesting point for debate was, however, whether one would expect the highest pressure which could be induced at any depth in such a way to be limited to the actual earth pressure at that depth. He personally was inclined to think that this would not be so, and he had been much interested, at the summer meeting of the Institution, to hear Captain Comins say that after a fairly wide survey of the subject he had not found any case in which reservoir "rock pressure" was greater than "earth pressure." The authors of the present paper emphasised the fact that maximum rock pressure at Khaur was approximately equivalent to "earth pressure," and so this formed no exception to the rule. Bearing these points in mind, it seemed to him that the remaining theory—namely, that dead-weight earth pressure

was capable in greater or less degree of direct application to the fluid contents of reservoir rocks—was the one which *at the moment, and on present evidence,* could most easily be given a very wide application. It seemed to him that one could imagine, firstly, cases in which the full pressure of the overlying strata could be transferred to the fluid contents of a reservoir ; secondly, cases where the rocks were of such a nature that earth pressure would have no effect on reservoir fluid pressure ; and, thirdly, all gradations intermediate between these two extremes. If this were so one would expect reservoir rock pressure (before withdrawal of fluids) always to lie between the limits of hydrostatic pressure of, say, ½ lb. to the foot of depth, and earth pressure of, say, 1 lb. to the foot of depth. It would, of course, be foolish to regard this as anything more than an interesting possibility until much more evidence of the type so clearly set out by the authors of this paper has been collected from different parts of the world and examined.

Mr. Ashley Carter said that, nowadays, the geologist located wells which had to be drilled to extreme depths ; there were two known at the present time which had been drilled to depths of upwards of 11,000 ft. Very high pressures were being encountered. It was only about twelve years ago that he happened to be on the Khaur field, and certainly none of the troubles mentioned were experienced at that time, but now that deeper drilling was being carried out they were being met with. It was also about that same time that the use of cast iron in valves and fittings for high pressures was to a certain extent superseded by the use of steel, because it was found that the pressures which had to be dealt with were such that they would entail extremely heavy castings in cast iron, and the stronger steel was substituted.

Metallurgy had played, and continued to play, and would always play, a very important part in the question of oil field development. An enormous amount of research work had been carried out and steel was graded. In their paper the authors gave three different grades of steel, and he found that there was a difference of well over 30 per cent. in the tensile strength of those three different grades which the authors mentioned.

Another very important point from the metallurgical standpoint, and one which was receiving a great deal of attention at the present time, was the resistance to corrosion. Certain waters had been mentioned that evening, and that again was a problem which was being attacked by the metallurgists, but there still remained a very great deal of work to be done in that direction.

In conclusion, he wished to congratulate the authors on the presentation of their paper, in which they described the extremely

economic and efficient methods which they adopted in order to solve the problems with which they had to deal.

Mr. Frank Dabell said the authors stated that there were in use the appliances of Kerotest, Shaffer, Doheny Stone, Seamark, Zublin, Martin Decker and others. He thought the least that could be said was that it would be good for national recovery. He could enlarge upon the virtues of these products, but he could also recite their failings. He thought, however, that such details were better left to branches where the majority of those present had an intimate knowledge of their working down to the smallest details, such as the way in which the mud-recording apparatus clogged and that the slightest failure of a valve to open fully led to serious trouble. He would confine himself, whilst paying the fullest tribute to the mechanical operation of the assembly of the various parts, to deprecating their multiplicity. The less number of joints the less risk of loss of control. The less obstruction to quick movement, the less risk to life, and the fact that presumably there was no loss of life must have been due to the men who assembled the parts.

He thought attention could usefully be centred upon the principles governing an operation of the kind in question, particularly if expressed by those dictating the policy. Recently he had heard Sir Thomas Holland say that it was the duty of the Council, parent or governing body, to discuss principles, that those principles might guide Committees in their work. Personally he thought that should be adopted to a great extent in the parent Institution ; principles should be discussed for the guidance of branches. On those lines he was tempted to ask what was gained by the imprisonment of the water ? No value appeared to be attached to the conserved power. No mention was made of the cost or time. He would point out that engineers, if they wanted to work in the bed of a flowing river, did not dam the river entirely but deflected part of it. The same applied to land slides. It was well known how Tom Sawyer conquered the difficulty of releasing an imprisoned negro ; he made him write a note in his blood and crawl through the roof, although the simple prisoner pointed out that there was egress through the door. He suggested it was possible that people undertaking such operations as those described in the paper followed the methods of Tom Sawyer. That was no reflection whatever on the authors. He was somewhat inclined to believe that perhaps one of them had in view warning others as to what rigid control meant and what it cost. That the authors did appreciate that aspect of the case is evident, because they hinted that the supply of water was not inexhaustible and referred to drilling special wells for the dissipation of the pressure. Nevertheless,

three hoists were used, and quite rightly used from Mr. Ward's point of view. Three hoists and presumably engines were occupied on the site of one test well. If that plant had been split up and relief pressure wells drilled in the vicinity, the work might have been done—he would not say it could have been done—in less time and without the transport to and assembly of the cumbersome parts referred to, in Himalayan regions. He was not attempting to put forward any better suggestion, but he did suggest that if research is to be done, it were better done in the direction of regulating release of pressure, and he suggested further that it might be on the lines of the reverse flush system of drilling, by which the pressure was released through the drill pipe. Above all it is to be remembered that in the majority of cases the relief of high pressure at depth is of volcanic nature in effect.

He wanted it to be clearly understood that he was not in any way belittling the mechanical operation described by the authors, which was perfect, notwithstanding the enormous number of connections and joints. With sand present, if one of them failed with 5000 lb. pressure, in thirty minutes there would not have been a derrick or anything else left standing.

Whilst he had concentrated on the main feature of pressure control, he thought one of the most interesting points in the paper was the origin of the pressure, and he thought the authors were entitled to a full report of views expressed on this point.

Mr. A. Millar said it would appear from the paper that at one time mud very heavily treated with barytes was used to control the pressures encountered. He would like to ask whether the authors experienced any difficulty in cleaning the wells of that mud. Also, he would like to know whether they used any method for the recovery of the barytes from the mud.

It was evident from the paper that the Zublin bit had again proved its high efficiency over the other types. Could the authors state the speed of rotation and weight in pounds maintained on the bits used when drilling through the sandstones and shales respectively ?

He would like to know what was the average footage of a bit in the sands above the oil-bearing rocks, and also through the shales.

It would be interesting to hear how the bits were dressed. He took it that some kind of hard facing material was used. What was the material used and was it put on by the use of the acetylene blow pipe or by the electric arc ? He would also like to know whether the heads were heat-treated from time to time.

The use of a perforated lining to form part of the drilling string was quite a novel method of overcoming the difficulty of setting

a liner. Could the authors give any information with regard to the type, size and number of perforations per foot in the liner? Was collared casing used? He took it that the annular space between the top of the liner and the casing was not sealed off.

The authors stated that the wells were produced either from between the casing and drill pipe or through the drill pipe. It would be interesting to know what the gas-oil ratios were? Would not it be better practice to use tubing and so release the drill pipe for further work, provided that a suitable high pressure head was available through which the drill pipe could be extracted and later the tubing inserted?

The fact that it had been found possible, by using high-pressure surface equipment, to drill and control the pressure met with without having to use barytes showed what could be done, and it was certainly a big step forward in the right direction.

Mr. J. Cuthill said that, in referring to the earlier efforts at high-pressure drilling the authors mentioned a stuffing box, and boxes of that kind were still largely in use. There was a question as to the limits of such a box in dealing with high pressure. He believed that the limit was somewhere round about 500 lb., and even then very considerable trouble was experienced in keeping the boxes in order. In addition to that, the vibrations of the drill pipe were communicated immediately to the casing, and that was one of the difficulties encountered at Khaur. He would like to hear Mr. Ward's opinion on that. It was mentioned in the paper that there was no method of running perforated casing through the stuffing box at the top of the well. That was so, but he would mention that a method of running perforated casing was described in one of the papers read before the World Petroleum Conference, where full details were given. He had no criticism to make, however, of the method adopted by Mr. Ward; it was an exceedingly interesting method, and the success of it was a proof of its value.

Mr. Ward mentioned the use of a trap for catching the cuttings under the enclosed system he had in use. He took it that only one trap was in use, a vertical trap of $8\frac{3}{4}$-in. casing with a 3-in. tube inside it. It seemed to him that that would be very small in capacity and that very frequent blowing out would be required. Was only one in use or was there a bank of them?

It was obvious that the trend of high-pressure control apparatus was towards a more flexible control head of the rubber packed type, in preference to the older types, which consisted of gates with comparatively small packings which might not effectively control the pressure. He would like to have Mr. Ward's opinion as to the comparative value of the two types.

Mr. Charles Dabell, referring to the theory mentioned by the President as to the origin of the high pressure encountered at Khaur, said it had occurred to him that sufficient study might not have been given to the possibility of the high pressure coming from below the oil sources. The President's hypotheses apparently dealt with the high pressures coming from above or possibly laterally.

One had very few, if any, figures with regard to the production of the undoubtedly expensive and deep well referred to in the paper. He was aware of the dangerously misleading nature of wells which came in with a huge rush, having dealt with one a few years ago which blew every tool out of the hole, ruined the derrick and itself. It was then decided to drill another well under rigid control. This was done ; signs of oil were encountered at the expected depth and the well was immediately capped. When the well was re-opened beyond a small amount of gas—with no pressure—nothing resulted, Well No. 1 having released all pressure.

Mr. A. P. Catherall said there were a number of remarks in the paper regarding the geology of the Khaur field and various theories had been brought forward, but he thought it might be useful if some further information was given with regard to the behaviour of the wells after they were brought in—i.e., the pressures, the gradual decline of pressure, if any, and the rate of decline of production over a period of time.

Mr. T. T. McCreath (Steel Brothers and Co., Ltd.) said he had been very glad to influence the writing of the paper and had encouraged the authors to publish it, because he thought the only way in which progress could be made in the oil world was by spreading the knowledge of the kind of difficulties that were encountered and the methods by which they had been overcome.

In many wells, dissipation of pressure had been tried, but then one went to another location and the pressure was still there. Even though there was a certain amount of dissipation in some places, it would be a very long time before it became general, and it was impossible to wait so long.

There was no secret about the position of and results from the well, as these had been referred to by the Chairman of the Attock Oil Company at the last General Meeting.

The objective of the well was the limestones which were estimated to be deeper than they proved to be. The consequence was that the well was cemented too deep in the limestones, and it was the opinion that a productive zone, considerably masked by the high-pressure control, had been cased and cemented off. It was therefore necessary to test it elsewhere.

It was very appropriate that Mr. Beeby Thompson should have read the paper that evening. Mr. Beeby Thompson was probably the man who had really made it possible to carry on the drilling in question, because, as was mentioned in the paper, the Zublin bit had made it possible to carry on with the high pressure work, and it was undoubtedly due to Mr. Beeby Thompson that the Zublin bit had been introduced. This he thought should really have been acknowledged in the paper.

Mr. E. S. Millar (Attock Oil Company) said that nobody wanted to drill under pressure, but the conditions were there and they had to be met. He thought Mr. Dabell's suggestion was to bleed sands and many other people had suggested that. A high pressure expert from the States had come over specially, and his theory also was to bleed while drilling was going on and to keep pressures off the casing heads. He could say that, owing to the peculiarities of the Khaur field and the heaving conditions due to allowing water to flow over the shales this was not practicable as a general policy. One or two wells had been lost trying it, and the company had been literally driven to drill under pressure and constant control. He thought that many other people might yet find the same conditions elsewhere in very deep wells as had been found at Khaur, and they would also be forced to pressure drilling or a closed system. He had been very interested in the remarks of Mr. Ellis with regard to a closed system for the mud.

His own company had been experimenting with that for some time, but the experiments had not gone far enough for it to be used in a well at Khaur. He thought, however, that there was a great future for that system if it proved feasible, because it would lessen the number of pumps required and ease the function the pumps were performing and cut out a great deal of wear and tear. Pressure drilling was only in its infancy, and there was a great deal yet to be found out about it.

With regard to rubbers, the greatest loss of time in drilling at Khaur had been due to rubbers. If there was any slight defect in the rubber, when it was necessary in an emergency to shut a gate, that gate was not 100 per cent. efficient, which, as it would be realised, it must be in high-pressure work. It was now understood that the lives of all the men working on the derrick floor might really be dependent upon the rubber. He could not pay too high a tribute to the brain that evolved the Seamark head. His company had had no trouble with Mr. Seamark's design, and he thought they never could have accomplished all that they had done, particularly in the tricky business of running a long string of casing under high pressure, if it had not been for Mr. Seamark's invention.

Mr. H. L. Ward, in replying to the discussion, said that methods had been used for the recovery of barytes from the mud.

With regard to the average footage of the bit, that of the fishtail bit was from 5 to 10 ft. With the Zublin bit there had been an average of not less than 50 ft. a hole at any time with one head, and the most that had been obtained, with a bit cutting a $14\frac{1}{2}$-in. hole, was 268 ft. The bit was redressed with manganese steel and ground off, and he thought 12 runs were obtained out of one head with the Zublin bit.

With regard to the perforated liners 3/16-in. holes were used, 4 in. apart.

Stuffing boxes of three decks were used, one screwing into the other, and when the rubber wore out another was screwed on.

There were two shale traps in operation at all times. A shale trap consisted of an 8-in. pipe, 10 ft. long, with a spring perforated on the inside with 3/16-in. holes, 2 in. apart. The circulation came in through the 8-in. pipe, and the mud fluid had to go through the perforations, the shale being caught in the trap.

With regard to the control head, considerable trouble was experienced with the rubbers, for the simple reason that the gas working into the pores of the rubber would cause a blister, and, on rotation, the blister would break. In such cases the fluid would usually come through, and, when it did under the pressures in question, it was almost impossible to get a valve acting in time to save the pressure on the well.

On the proposition of **The President,** a hearty vote of thanks was accorded to the authors of the paper and to Mr. Beeby Thompson for reading it.

Mr. C. E. Keep, in reply, wrote :—

I wish to take this opportunity to thank Mr. Beeby Thompson for so kindly reading the paper, and the members present at the meeting for the reception accorded to it.

The President has advanced a new theory for the origin of the high rock pressures of Khaur—namely, that it may be intrusive from below. I have not a copy of Mr. Anderson's paper available here, but so far as I remember no highly saline water was encountered in the Jhatla well. However, it is clear that the Khaur brine is not indigenous to the Murrees, but has a deeper source, and it is therefore quite likely that the pressure under which the fluid is now found in the Murrees at Khaur is imposed from greater depth.

As a result of the discussion, we may now rule out the theory of inherited pressure. so far as Khaur is concerned, but Mr.

Dewhurst's hypothesis replaces this and we are still left with the choice of three theories.

Mr. Abraham favours the earth pressure theory. I do not think, however, that I laid great emphasis on the fact that the rock pressure at Khaur is actually the earth pressure. What I wished to emphasise was that the similarity between the earth pressure and the rock pressure may be purely a matter of coincidence. I would not suggest that the highest pressure which could be induced by compressional strains in the rocks is limited by the actual earth pressure. It may be pure coincidence that the highest rock pressure yet recorded at Khaur is slightly less than the earth pressure. It must be remembered that the Khaur anticline is peculiar among oilfield structures in that the folding system of which it is a part is one of great intensity and one that is still being developed at the present time. I account for the lower pressures of Jhatla by reference to the facts that the folding in the vicinity of Jhatla is relatively very gentle, and that partial relief of pressure may have been obtained there by the escape of fluid up dip, at the foot of the Salt Range.

Mr. Frank Dabell has discussed the possibility of relieving the pressure before attempting to drill through the high pressure zone. Had the cost and hazards of drilling relief wells, and the time taken in doing so, not been so great, there is little doubt that the regulated dissipation of pressure would have proceeded to a much more advanced stage before the decision was taken to drill through the zone. Pressure drilling, against high pressure, is very costly and very hazardous, but there are times when it becomes necessary to adopt such measures.

I agree entirely with Mr. Ellis's advocacy of closed mud circulation. At the Summer Meeting, in discussing his previous references to this method, I ventured to say that : " Presumably it is only a question of time until all the snags are eradicated from the method, and closed circulation becomes widely adopted in practice." At the time of the drilling of the Khaur Deep Test, the snags had not been eradicated, and we did not feel justified in experimenting with the method, although it was actually considered. It is very satisfactory to learn that closed circulation has recently been in successful operation for some months. Mr. Ellis has undoubtedly done a great service to the industry by stressing the possibilities of the method, and it is much to be hoped that it has now come to stay.

Mr. Ashley Carter's reference to the part played by modern improved equipment in combating difficult drilling problems is apposite and timely. In the drilling of the Khaur Deep Test, the control pressures used approached very closely to the rated

test pressure of the fittings. The safety of the men on the well, and the successful completion of the operations, were both dependent on the reliability of the equipment. A tribute to the metallurgists and manufacturers is thoroughly well deserved.

The question of difficulty in cleaning wells in which heavy barytes mud had been used, raised by Mr. Albert Millar, cannot be simply answered. I think that all too frequently barytes is blamed for clogging sands on the grounds that wells often continue to show barytes weeks or months after they are put on production. The distinctive colour of barytes makes its presence in the production evident. Clay mud is generally composed of finer material than barytes, and would therefore be expected to penetrate further into the sands, but as the clay particles show only as a slight discolouration in the production they are not blamed for any disappointing results given by the well. The possible clogging of sands by barytes could well become a subject of special study.

The perforated casing used at the bottom of the drilling string, in Mr. Ward's method, consists usually of collared pipe ; in fact, it is only in the smallest size of hole that anything else is used, $3\frac{1}{2}$ in. inserted joint casing having been run inside $4\frac{1}{2}$ in. and $4\frac{3}{4}$ in. casing. The annulus between the top of the liner and the casing is not sealed off.

Admittedly it would be better practice to flow the wells through tubing, rather than through the drill pipe or between drill pipe and casing, given a suitable head, but there is a point at which one must be prepared to sacrifice part of the efficiency for the sake of safety and of simplicity.

Several speakers have commented on the omission of information regarding the production histories of the wells, pressure declines, gas-oil ratios and similar data. In reply to this, I would point out that the paper was primarily written as an account of particular drilling operations.

The Action of the Silent Electric Discharge on Hydrocarbon Gases and Oils.*

By A. W. Nash, M.Sc., F.C.S., M.I.Mech.E. (Member), J. L. Howard, M.Sc., and F. C. Hall, B.Sc.†

Introduction.

Interest has been aroused during recent years on the action of the silent electric discharge on oils, due to reports that have been published from time to time on the value of this action in modifying the properties of lubricating oils, for example in the case of certain oils for aero engine lubrication. As facts about the economics of this method of treating oils are difficult to obtain, the following article indicates the scientific aspects only, and is an attempt to correlate the published accounts of experimental work bearing on this subject which have hitherto been somewhat scattered and difficult to assess without presentation in a collected form.

From the theoretical viewpoint, the most interesting field lies in the action of the discharge on pure hydrocarbons and their derivatives, for it is from study of this that light has been thrown on the action of the discharge in general. Accordingly, this aspect will be considered first.

The Action of the Silent Electric Discharge on Gaseous Hydrocarbons.

The silent electric discharge[1] is generally considered to take place between two electrodes, separated by a gaseous medium, at a high potential difference which is, however, below the sparking potential. The potential is usually alternating and the discharge, at atmospheric pressure, has received different names according to its appearance.

In the silent discharge in an ozoniser, the electrodes are usually covered with a glass dielectric and the current passing is small. If one or both electrodes are in direct contact with the gas, then we have the so-called semi-corona and corona discharges, or brush discharge, and the current passing may be considerably greater.

At lower pressures, the phenomena of the gaseous discharge tube appear, and the production of electrons, with consequent current density, may be high. It has been stated[2] that this type of glow discharge more nearly approximates to an arc, in its effects, than to the silent discharge. The action of different types of discharge consequent on different potentials, densities and

* Paper received March 4th, 1934.

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frequencies of the current, and on the pressure of the gaseous phase, has been discussed by Peters[2] (*cf.*, Lind and Glockler).

Before reviewing the action of the discharge on individual classes of hydrocarbons, it may be mentioned that much of the recent work in this sphere has arisen from investigation of the phenomena of Corona wax. It has been found that, while hydrocarbon oils are stable to electrical stresses in the absence of any gaseous phase, if gases are present then the oils tend to deposit an insoluble waxy substance—Corona wax—which interferes greatly with the insulation of cables, etc., impregnated with the oil.[3] The action is due apparently to bombardment of the liquid dielectric with gaseous ions and electrons, and investigation of the phenomena has proceeded along two distinct lines : the reactions of hydrocarbons under electrical discharge, and the change in electrical characteristics of oils, etc., under the corona discharge.[3,4,5]

The earliest recorded work appears to be that of Thenard,[6] who observed that ethylene condensed to a powerfully odorous liquid when passed through an ozoniser. In the same year, Berthelot[7] showed that many organic substances yielded acetylene under the influence of the silent discharge, and in addition found that methane, ethane and ethylene gave hydrogen together with resinous condensation products. The action of the discharge was thought to be analogous to that of thermal treatment, but it has since been recognised that the two effects differ widely.

Action on Paraffin Hydrocarbons.

As mentioned before, Berthelot[7,8,9] obtained from methane a condensation product, of empirical formula $C_{10}H_{18}$, together with hydrogen and acetylene, while similar products were also obtained from ethane. He found the nature of the reaction to depend on the intensity of the discharge, and in each case the amount of hydrogen liberated to be equivalent to the amount of hydrocarbon decomposed. Prolonged treatment was found to polymerise the acetylene first produced, and Berthelot recognised the complexity of such reactions in which the primary products themselves decomposed under the action of the discharge.

Lind and Glockler[10] submitted the four lowest members of the paraffin series to the action of a semi-corona discharge, and found them to condense to complex solid and liquid hydrocarbons, with elimination of hydrogen and, in the case of the higher members, some methane.

The formation of methane had been noticed previously by Losanitsch[11] while working with *iso*-pentane and *n*-hexane. Using an ozoniser type of discharge, Lind and Glockler[12] showed that the four hydrocarbons, previously treated, underwent the same general

pressure change with time, and found that all the liquid products had the same general formula, C_nH_{2n}. The formation of unsaturated gaseous products in the intermediate stages was noticed.

From ethane[13,14] they were able to produce a liquid whose molecular weight could be kept between 105 and 417 by controlling the time of treatment of the primary products. The gaseous products contained hydrogen, methane, propane, butane and pentane.

One of the lighter fractions of the liquid polymerised from butane was studied in detail[15] and found to be chiefly a mixture of octanes and octenes, formed by simple doubling of the butane molecule with elimination of hydrogen. Becker[16] has also found that the higher paraffins, in the silent discharge, may condense in this manner.

In line with this may be mentioned the work of Schoepfle and Connell,[3] who studied the gaseous products evolved from hydrocarbon oils under cathode-ray bombardment, and of Schoepfle and Fellowes,[4] who extended the investigations to a number of pure hydrocarbons. It was found that only saturated oils and compounds evolved any quantity of hydrogen under the experimental conditions.

The action of the silent discharge on heptane has been described by Christen,[17] with analysis of the gaseous products, while Linder[18] has studied the rate of evolution of gases from the vapours of different hydrocarbons, from *n*-pentane to tetradecane.

Recently Saint-Aunay[19] has investigated the action of the silent discharge on hydrocarbon vapours with a view to obtaining more selective reaction. Careful control of temperature and intensity of the discharge led to products whose formation could be represented by a fairly simple mechanism. Briefly, the reactions are divided into three classes :—

(1) Polymerisation, due to activation of C—H linkages in *unsaturated* compounds.

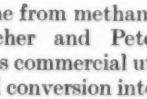
(2) Dehydrogenation, observed with all hydrocarbons except acetylene, due to activation of C—H linkages, the intensity increasing with degree of saturation of the hydrocarbons.

(3) Decomposition, due to rupture of the C—C linkage, notably in long-chain hydrocarbons.

Methane was found to give quantities of hydrogen and smaller amounts of ethane, ethylene and acetylene, with a small quantity of an olefinic liquid. The basic reaction is dehydrogenation to active radicals which condense to ethane : this then undergoes further reaction. Ethane gave similar products, including methane, while hexane yielded considerable amounts of liquid products

containing hexene–1, higher saturated paraffins (C_9 and C_{12}), and cyclic compounds. The gases produced included propane and propylene.

Brewer and Kueck[30] have obtained almost complete conversion of methane into ethylene and hydrogen in the glow discharge at very low temperatures. At higher temperatures Peters and Wagner[21] find spectroscopic evidence for the reaction :



The production of acetylene from methane in the silent discharge has been studied by Fischer and Peters,[22] and Peters and Pranschke,[23] with a view to its commercial utilisation. At pressures of 15–50 mms., they obtained conversion into almost pure acetylene, finding that the use of diluted methane inhibited carbon deposition.[22]

Peters and Wagner[24] have investigated the formation of ethylene from mixtures of methane and hydrogen, finding that low pressures reduced the amount of acetylene formed ; the conversion of methane with steam and carbon dioxide in the silent discharge is described by Peters and Pranschke.[25]

The action of the discharge on coke-oven gas has been described by Pieters[26] and by Peters and Neumann.[27] The latter used a discharge of high density with a view to the production of acetylene, which was then catalytically converted into liquid products.

The application of the silent discharge to the detection and estimation of methane is discussed by Erlwein and Becker.[131]

Among patents in this field may be mentioned two held by Epner, claiming the production of fuels from methane and other hydrocarbon gases with[28] and without[29] catalysts. Recently the formation of aldehydes from methane and carbon dioxide has been patented.[30]

Action on Olefine Hydrocarbons.

The action of the silent electric discharge on ethylene and other olefines has been the subject of considerable research. Thenard[6] and Wilde[31] found that ethylene condensed to a strongly odorous liquid, and Berthelot[9] noted the production of acetylene. Collie[32] obtained hydrogen and a liquid polymerisation product of olefinic character.

Losanitsch and Jovitschitsch, individually and together, investigated the condensation of ethylene, using low voltage discharges,[33,34,35,36] and also low pressures[37] ; they were unable to

account for an apparent disappearance of carbon during the condensation.

Lind and Glockler[10] found the condensation products of ethylene to resemble those from paraffin hydrocarbons, but to have a general formula of $C_nH_{1.8n}$. The products were compared with those obtained under alpha-ray bombardment.

A yellow mobile oil of molecular weight 215, consisting of unsaturated hydrocarbons from C_6H_{12} upwards, along with saturated hydrocarbons, was obtained from ethylene by Demjanov and Prianishnikov,[38] while Mignonac and Saint-Aunay[39] obtained nearly 90 per cent. conversion into butene–1 and hexene–1. They considered that ethylene molecules, activated by the discharge, condensed with unactivated molecules. Szukiewicz[40] has also obtained about 60 per cent. conversion of ethylene into butylene with production of an equilibrium concentration of 18 per cent. acetylene in the gaseous phase. Under different conditions the formation of butadiene was also noted.

According to recent work by Saint-Aunay,[19] there are three reactions taking place under their experimental conditions : (1) polymerisation to butene–1 and hexene–1 ; (2) dehydrogenation to acetylene and hydrogen ; (3) hydrogenation by the hydrogen liberated in (2) to give ethane, butane, etc.

Vernazza and Stratta[41] have also studied the polymerisation of ethylene with reference to the formation of acetylene.

On investigating the hydrogenation of ethylene at low pressures, Volmar and Hirtz[42] found the chief gaseous product to be methane. The primary reaction was considered to be disruption of the ethylene molecule at the double bond, followed by reactions of the liberated radicals.

Propylene was found by Berthelot[9] first to condense rapidly to a liquid with elimination of hydrogen, and then to a solid of composition $C_{15}H_{26}$; a similar liquid was obtained from trimethylene. The condensation of propylene and *iso*-butylene has been investigated by Demjanov and Prianishnikov.[38] The product obtained by these investigators from isobutylene[43] had an average molecular weight of 140 and consisted chiefly of the hydrocarbons C_8H_{10} and $C_{12}H_{24}$. The process was considered by Prianishnikov to be partly one of redistribution of hydrogen atoms with polymerisation, accompanied by fission and rearrangement of alkyl groups.

Amylene vapour, under the discharge, was found by Meneghini and Sorgato[130] to yield an unsaturated condensate with acetylenic gaseous products ; in contrast to Becker's conclusions,[16] they found the initial presence of hydrogen essential for the production of saturated compounds.

Among patents on the utilisation of olefines in this manner may be mentioned those held by Epner[45] and the I. G. Farbenindustrie A.-G.,[46] who claim conversion of cracking gas into lubricants. Thomas[47] claims stabilisation of cracked spirits by polymerisation of the unsaturateds in the silent discharge.

Action on Acetylene Hydrocarbons.

The discharge has a profound effect on acetylene. Wilde[31] observed that it was completely condensed in an ozoniser to a yellow oil, which on standing gave an amorphous brown solid, while Schutzenberger[48] obtained a yellow resinous solid analogous to that from benzene.

Berthelot,[49,9] Losanitsch[36] and Jackson and Laurie[50] examined the condensation products from acetylene, finding the solid to be insoluble and unstable to heat. Both solid and liquid products readily absorbed oxygen from the air. According to Losanitsch, the presence of water in the original acetylene leads to formation of polymers of acetaldehyde (*cf.*, *Löb. Ber.*, 1908, **41**, 87).

The molecular weight of the liquid, freshly prepared at low temperatures, was found by Kaufmann[51] to be 226 rising to 266 after several hours. It had the empirical formula $(C_2H_2)_n$ and was produced at the rate of 30–50 gm. per hour. At higher temperatures, the product from the discharge was a pale yellow insoluble powder. A similar product was obtained by Coolidge[52] using high-speed cathode rays.

Mignonac and Saint-Aunay,[53] working at −60°, prepared a liquid containing a trimeride of acetylene and a low boiling point hydrocarbon. Under certain conditions they obtained a mixture of dipropargyl, γ-methyl-$\Delta^{\alpha\beta}$-penta-diine and diethenylacetylene, and considered that ethinylethylene was formed as an intermediate. Recently, Saint-Aunay[19] has shown that the basic reaction of acetylene under a carefully controlled silent discharge is one of polymerisation to the trimers: dipropargyl $(HC{\equiv}C-CH_2)_2$, methyl pentadiine, $CH_3-CH\ (C{\equiv}CH)_2$, and divinyl acetylene $(H_2C{=}CH-C{\equiv})_2$.

While studying the spectra of the glow discharge in acetylene, Harkins and Gans[54] observed the condensation to a flaky brown product, analogous to that from benzene. (*Cf.*, Austin.[55]) Acetylene has been subjected to the discharge in the presence of hydrogen by Berthelot[8] and by Losanitsch,[36] who found absorption of hydrogen. Under similar conditions, Volmar and Hirtz[42] obtained saturated hydrocarbons up to C_8 together with acetylenes and olefines. The presence of methane indicated rupture of the double bond in the case of some of the acetylene molecules.

Allylene has been condensed by Berthelot[9] to a solid with a pungent, acrid odour.

Action on Cyclic Hydrocarbons.

According to Becker,[16] cyclic hydrocarbons, under the silent discharge, behave in a complex manner, to give mixtures of saturated and unsaturated compounds, formed from degradation products of the original hydrocarbons.

Schutzenberger[48] obtained from benzene a yellow transparent resin resembling that from acetylene. Losanitsch[37] studied the action of the discharge at low pressures on benzene (and other aromatic hydrocarbons) and diphenyl was obtained on distillation of the condensation product. Recently, Davis[56] has obtained diphenyl from benzene with considerably lower production of hydrogen than that theoretically possible. A part of the hydrogen was apparently used up in hydrogenating other reaction products.

The production of a viscous black liquid and solid was observed by Jovitschitsch,[33,35] with an unexplained deficiency of carbon and hydrogen. Using a semi-corona type of discharge, Jakosky[58] obtained from benzene, in the vapour phase, a brown liquid with an odour similar to that of pinol, which on oxidation with ozone yielded crystals of a terpene derivative.

An insight into the mechanism of the process was obtained by Harkins and Gans,[54] who examined spectroscopically the decomposition of benzene vapour in the discharge. They found lines due to molecules of carbon, radicals (CH), and atoms of C and H, and these apparently combined completely to give a brown flaky deposit, formation of gaseous products being practically nil. (*Cf.*, Austin.[55])

Saint-Aunay[19] has found that under suitably controlled conditions, benzene undergoes three basic reactions : (1) polymerisation to dihydro-diphenyl ; (2) dehydrogenation to give diphenyl and hydrogen ; (3) depolymerisation to give C_2H_2 with rupture of C–C linkages. The hydrogen liberated in (2) can hydrogenate the acetylene to ethylene and ethane, the formation of considerable quantities of gaseous products being noteworthy. Analogous reactions were found for toluene.

According to Berthelot,[8] benzene absorbs hydrogen under the discharge to give a polymer of C_6H_8, oil of turpentine under the same conditions giving a resin. Becker[16] showed that tetralin reacted with the nitrogen of air to give hydrogen cyanide and other compounds, and with hydrogen to give a colourless semi-solid resin. A similar product was formed from decalin.

The reaction of nitrogen with various hydrocarbons under the silent discharge has been the subject of some investigation, and reference may be made to the work of Berthelot,[9,56] Briner and Durand,[44] and Miyamoto[59] in this connection.

General.

A number of papers have appeared in which the theoretical principles involved are discussed.

Lind and Glockler[12,13] have shown the close resemblance of these gaseous reactions, under the discharge, to those produced by ionisation due to alpha rays,[60] and have applied similar reaction mechanisms. Lind[61] has summarised the theories put forward, as follows : (1) photochemical reaction due to the ultra-violet light from the discharge ; (2) kinetic-ion theory, according to which the gaseous molecules react, due to their activation by electrical (and thermal) energy ; (3) static-ion theory,[62] in which the reactions are considered due to combination of positive and negative ions in the gas (and not at the electrodes).

The Kinetic-ion theory has been investigated by Elliott, Joshi and Lunt,[63] who developed an expression for the velocity of reaction in terms of the gas pressure, field strength, current density and critical energy of activation of the gas molecules.

Support for the static-ion theory is found by Lind and Glockler, who envisage reactions between ion clusters in addition to ions. The simple butane condensation is suggested[15] as :—

$$C_4H_{10} \longrightarrow C_4H_{10}^{+} + \bar{E} \quad \text{ionisation.}$$

$$C_4H_{10}^{+} + C_4H_{10} \longrightarrow (C_4H_{10}.C_4H_{10})^{+} \quad \text{ion cluster formation.}$$

$$(C_4H_{10}.C_4H_{10})^{+} + \bar{E} \longrightarrow C_8H_{18} + H_2 \quad \text{ionic combination.}$$

They consider polymerisation followed by elimination of simple components to be more likely than initial disruption with subsequent condensation.

In this connection, Lind and Schultze[64] have studied the influence of pressure and time on the decomposition of methane, ethylene and acetylene, while Lind, Marks and Glockler[65] have followed the reactions of the lower paraffins, under cathode-ray bombardment, by the evolution of hydrogen. (*Cf.*, Schoepfle and Fellows.[4]) A relationship was found between the molecules reacting and the ion-pairs present. Brewer and Kueck[20] find in the condensation of methane that a molecule of ethylene is formed for every $(CH_4)^{+}$ ion.

The rate of evolution of gaseous products from higher hydrocarbon vapours, under the silent discharge, has been investigated by Linder,[18] who found that in at least one case a law analogous to that of Faraday was being followed. Linder and Davis[66] have put forward a theory of the reactions involved in the glow discharge in which primary reactions are considered due to collision of

molecules with positive ions (and activated molecules) and to dissociation of activated molecules.

The Action of the Silent Electric Discharge on Fatty Acids and Oils.[67]

The action of the discharge on fatty acids and oils is of interest in that light is thrown on the mechanism of the Electrion and Voltol processes for the production of lubricating oils.

De Hemptinne,[68] in 1905, patented a process for the hydrogenation of oleic acid in the silent discharge. This was later extended by Wielgolaski,[69] Walker[70] and Utescher[71] to oils, fats and waxes in general. In connection with this may be mentioned the investigations of Custis,[72] Elliott[73] and Chalerier,[74] among others, on the hydrogenating power of hydrogen activated by the electric discharge.

Eichwald[75,76] found that if oleic acid was treated in an atmosphere of hydrogen, nitrogen or air, the iodine number fell while the molecular weight increased considerably. The stearic acid content rose, with fall of iodine value, to a maximum or equilibrium value. He concluded that hydrogen was split off from the oleic acid molecules by electronic bombardment, leaving unsaturated residues. The liberated hydrogen saturated the double bonds of other oleic acid molecules to give stearic acid, while the unsaturated residues polymerised to molecules of high molecular weight.

On treating glycerides of fatty acids, Eichwald found that the glyceride portion of the molecule was unaffected ; the resultant oils, having high viscosities and flat viscosity-temperature curves, were good lubricants.

The deodorisation of fish oils in the discharge was patented by De Hemptinne[77] ; investigating this for cod-liver oil, Iwamoto[78] obtained considerable rise in density and refractive index, with fall in the iodine value and deodorisation of the oil.

The same investigator,[79,80] working with various unsaturated fatty acids, studied their hydrogenation and polymerisation under different conditions. The effect of various catalysts on the hydrogenation and polymerisation of oleic acid was also investigated,[81] bismuth oxide and ferric chloride being found effective in polymerisation.

Applying the discharge to rape oil, Hock[82] obtained, in addition to a more viscous oil, a yellow spongy insoluble deposit, which was suggested as being suitable for a rubber substitute.

Slansky[83] has discussed the action of the silent discharge on vegetable oils and resins, with particular reference to their use in the paint and varnish industry. In this connection may be mentioned a patent[84] for the improvement of drying oils by subjecting them to the action of cathode rays.

The Production of Lubricating Oils by the Electrion and Voltol Processes.

De Hemptinne, while investigating the hydrogenation of fatty oils in the silent electric discharge, observed that the oils increased in viscosity. Continuing investigations with the Belgian firm of Cavel et Roegiers, in 1909 he obtained his basic patents[85] for the production of lubricants by the action of the Silent Electric Discharge, and it is stated that in 1912 these Electrion oils were in commercial production at the Ghent factory. It was proposed to commence with a 50 per cent. fatty-oil-mineral oil blend, increasing the mineral oil content during the electrical treatment till the final product contained only 15 per cent. fatty oil (Otto). The apparatus patented by De Hemptinne was essentially a horizontal cylindrical drum with scoops around the inside periphery. The drum rotated about a horizontal axis and the scoops then caused the oil, contained in the drum, continuously to drip over the electrodes in the centre of the apparatus.

After the outbreak of War in 1914, Germany took over the Ghent factory and later established similar ones elsewhere. Under Nernst, a factory was erected at Potschaffle in 1917, known as the Deutsche Electrion Oel Gesellschaft, and in 1918 this produced 1650 tons of lubricating oil for aeroplanes. Due to shortage of fats, this oil was produced from mineral oils and proved a satisfactory substitute for castor oil.

After the War, Cavel et Roegiers re-acquired the production and selling rights of the Electrion oils, while the German firm retained German patents and was renamed the Deutsche Voltol Oel Gesellschaft, producing the Voltol oils.

Improvements in the original De Hemptinne process were claimed by the Continental Caoutchouc and Gutta Percha Co.,[86] who used catalysts in the process, and by the Gruner patents[87] in which the use of an acid atmosphere was proposed.

In 1923, Hock[88] published an account of investigations into the chemical and physical properties of oils produced from fish oils by Voltolisation, and described their production. Fish oils were treated in an atmosphere of hydrogen at low pressures and at a temperature of 60–80°, with a discharge due to a current of 4000 volts at 500 frequency. After several hours the oil had reached maximum viscosity and was known as "Half-Voltol." Addition of an equal volume of mineral oil followed by further treatment gave a very viscous product—"Full-Voltol."

The production of satisfactory lubricating oils from blends of voltolised fatty oil with mineral oil was confirmed by the work of Eichwald,[75] who also applied the process to crude low-temperature tars.

In 1925, Isom[89] described the process of voltolisation carried out at the Deutsche Voltolwerke A.-G. plant at Potschaffle, and outlined the history of the process. Due to the slow voltolisation of mineral oils, in the commercial process, rape-seed, cotton-seed or fish oils were first voltolised till they reached maximum viscosity, then 50 per cent. of a pure mineral oil (American 500 Red) was added slowly during continuous treatment till the viscosity approached 40° E., at 100° C. A similar type of converter to that described by Hock[88] was used, the pressure being 60–65 cms. of mercury with no hydrogen initially present. The current used was 23 amps. at 4600 volts and 500 frequency, with a temperature of 80° C.

The possibility of treating the oil converted into a froth, by counter-current flow of some inert gas, was being investigated and in this connection may be mentioned two patents held by Vogel for such a process.[90]

Rabek[91] has described a process for the polymerisation of mixtures of mineral and vegetable oils in the high-frequency discharge, while Becker[16] has studied the mechanism of the polymerisation of the higher paraffins.

A number of reviews and accounts of Voltolisation and Electrionisation have appeared in the technical literature.[92,93,94,95,96]

Otto[97] and Wolf[96] give details of the manufacture of Voltol oils by the Rhenania Ossag Mineral Olwerke A.-G. at Hamburg, and at Dresden. The process was similar to that at Potschaffle, except that an atmosphere of hydrogen was used. Commencing with a fatty oil, they worked up to a final product containing 90 per cent. mineral oil, having a viscosity of 90° E. at 50° C. They also prepared a base of voltolised oil which could be blended in amounts up to 25 per cent. with straight mineral oil, to give satisfactory lubricants needing no further treatment. The plant at Dresden was a modification of the original De Hemptinne apparatus with a capacity of 900 cu. ft., and is described in German Patent, 234,543.

Roegiers[98] has described the development of the Electrion process at Ghent, giving characteristics of the oils obtained, while Ullan,[99] in an account of the Voltol process, discusses the use of inferior fatty oils (*e.g.*, olive) as a basis for the production of satisfactory lubricants.

Among recent patents dealing with the Voltol process are two held by the I. G. Farbenindustrie A.-G.,[100] who carry out the process in the presence of powdered coal, etc., and claim economy in time thereby. The same firm claims the production of lubricating oils by treatment of alkylated naphthalenes[101] or halogenated paraffins[102] in the silent discharge.

Attention has also been directed to the tars obtained from the large lignite deposits in Germany. Eichwald[103,104,75] applied the Voltol process to crude low-temperature tars, and found the product to be more saturated and to have less tendency to resinify, thus resembling a mineral oil more closely.

The I. G. Farbenindustrie A.-G.,[100] describes the treatment of a middle fraction of a cracked brown coal tar of viscosity 1·2° E., at 12,000 volts and 7000 cycles to give a product of viscosity 125° E. The same firm[105] claims the production of viscous lubricants from hydrogenated and cracked coal tar, etc.

An interesting application of the Voltol process, described by Otto, is the production of transformer oils from Russian and New Jersey kerosines.

The mechanism of the Electrion and Voltol processes has been investigated by De Hemptinne and by Nernst,[96a] who concluded that electronic and ionic bombardment of the oil, under the discharge, split off hydrogen leaving unsaturated residues. These residues then polymerised to molecular complexes of considerable size. As mentioned before, Eichwald found that an entirely analogous reaction took place during the hydrogenation of oleic acid in the silent discharge. The colloidal character of these voltolised oils has been investigated by Hock with the aid of ultra-filtration.

Properties and Utilisation of Electrion and Voltol Oils.

Apart from the increase in viscosity, the oils produced by this electrical treatment have certain distinctive properties. The most striking feature is their low viscosity-temperature coefficient. The following figures for Electrion oils are given by Roegiers.

Oil.	Viscosity at 100° C.	50° C.	20° C.	Solidifying Point.
Russian	1·65° E.	6·5° E.	43° E.	—18° C.
Mid-Continent (U.S.A.) ..	1·69° E.	6·5° E.	41° E.	0°
Electrion A.	1·95° E.	6·5° E.	33° E.	—28°
Electrion B.	2·15° E.	6·5° E.	28° E.	—15°

This property of a flat viscosity-temperature curve is now recognised as of great importance in the lubrication of internal-combustion engines. Lubrication and starting-up in the cold are improved, while the enhanced viscosity when hot results in better lubrication with reduced leakage of oil past the piston rings.[106]

These oils are considered to have greater oiliness than straight mineral oils. Isom[89] quotes from a report of the Deutsche Voltolwerke A.-G., who find that Voltol oils adhere to metal surfaces, under conditions of extreme pressure, temperature and velocity, more firmly than do mineral oils. Otto[97] states that friction losses in machinery lubricated with Voltol oils are unusually

low, while heat development may be reduced by 50 per cent. This aspect has been discussed by Wolf[96,107] at some length. The high degree of oiliness exhibited by these oils has been attributed to their large molecular volume and weight.[96,106,108]

The behaviour of Voltol oils in automobile engine lubrication has been investigated by Becker,[109] while Electrion oils are stated to be particularly suitable for aircraft and to be recommended by prominent aero-engine manufacturers. In connection with this it is stated[92,94] that Voltol oils were used for the Transatlantic flight of the Zeppelin ZR3 to America, and in the airship Norge during Amundsen's flight to the North Pole.

Electrion and Voltol oils are stated to be very stable to heat and oxidation, and to deposit very little carbon in the combustion chamber, or sludge in the oil sump. According to Isom and Wolf, such properties of an oil as asphalt content, cold test, acid number and colour, are little changed on voltolisation, but the characteristic " voltol odour " is always acquired.

These oils have been found to be readily emulsified with water alone, and hence are of value in the lubrication of steam cylinders.[96] Vincent[110] states that the use of emulsified oil containing 5 per cent. Voltol has resulted in a saving of 50 per cent. in certain steam engines. These emulsifying properties are utilised in grease manufacture in a recent patent[111] (see also Otto).

The Silent Electric Discharge and Vapour-Phase Cracking.

The silent discharge has been used to promote the cracking of hydrocarbon oils, its value seeming to lie in its physical rather than on any chemical effect on the oil vapours.

In 1915, Davidson and Ford[112] claimed conversion of hydrocarbon gases, under the discharge, into those of lower molecular weight, while Robertson[113] obtained cracking of crude oil vapours with increased gasoline yield. Cherry, in 1917 and 1920, took out three patents,[114,115,116] which have been the basis of most of the commercial work since then. The first claimed molecular rearrangement and hydrogenation of hydrocarbon vapours, under a high frequency oscillating discharge, yielding products of different gravity and boiling point; the two later patents dealt with types of apparatus employed. An account of experimental results for a kerosine in the presence of natural gas has been published.[117]

The effect of the corona-discharge on cracking was studied at some length by Jakosky[58] at the U.S. Bureau of Mines. Using both high and low frequency discharges, applied to the oil vapours in a cracking tube, he found the discharge to be without effect

at temperatures below 600°. Above this, both the yield and the degree of unsaturation of the light products were increased, the high frequency discharge proving most effective.

Investigating the action of the discharge, Jakosky observed that below a certain critical temperature the oil vapours existed in the form of a mist; application of the discharge caused precipitation of the mist against the walls of the cracking tube. Above this critical temperature, the vapours existed as a gas and were not visibly affected by the discharge.

On the basis of this, he concluded that the effect of the discharge in promoting cracking was due almost entirely to two factors. Firstly was the precipitation, by the discharge, of the heavier components of the vapour, existing as a mist, against the hot walls of the cracking tube, thereby causing more efficient cracking. In this respect the action resembled that of the Lodge-Cottrell dust-precipitator. Secondly, of less importance, was the reduction in channelling of the vapours, giving rise to better heat transfer.

The chemical action of the corona on the gaseous hydrocarbons was comparatively slight, in keeping with the low energy associated with it.

Jakosky holds two patents[118,119] for the utilisation of the discharge in cracking and has suggested its use for increasing the efficiency of different types of condensers, based on the precipitating action described.

The combined hydrogenation and cracking of hydrocarbons in the discharge is claimed by Northrup,[120] while Feige[121] uses oils containing pulverised coal and metallic catalysts. The vapour from the distillation of solid fuels, such as coal and lignite, may be similarly treated.[122] and the use of ultra-violet light, in addition to the silent discharge, has been patented.[123] By the use of a superposed D.C. current on the usual high frequency discharge, the Aktis. A.-G. claim[124] hydrogenation of heavy oil vapour in the presence of superheated steam. The presence of oxidising agents in the still preparatory to electrostatic cracking has also been proposed.[125]

Rowland, working with the C. and C. Developing Co., has developed a cracking process[126] utilising the silent discharge. Of two papers published, the first[127] dealt with the types of cracking stock used, while the later one[128] refers also to the theoretical side of the process. He states that after years of research, based on the Cherry patents, motor fuels are now (1931) being made in this way. The difficulties encountered in producing suitable insulation, and in raising the process efficiency, are described.

Rowland outlines theories put forward to explain the action of the discharge and indicates his own views. He considers it

possible for an electron moving through the vapour to carry with it, or before it, a molecule of the vaporised hydrocarbons. On reaching a surface capable of absorbing the electron, the impact may be great enough to disrupt the molecule, particularly if, as is the case, the surface is very hot.

The gasoline produced by this process is stated to need no blending, being highly satisfactory from the point of view of anti-knock value and mileage figures.

It is relevant to mention here a recent patent held by Egloff[129] for desulphurising cracked hydrocarbons by treatment of the vapour with ozone and the silent discharge.

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Isolation of a Natural Inhibitor from Rumanian Cracked Distillate and Its Application to Selective Acid Refining.*

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Summary.

1. Results of the fixed time Voorhees and Eisinger gum test on a Rumanian Dubbs cracked gasoline, treated with 2 per cent. sulphuric acid at a mixing time from 5 to 300 seconds, are given.
2. Results of the copper dish gum tests are given for the same samples.
3. The effect of soda and doctor treatment on the 198° C. F.B.P. fractions of the pressure distillate, treated as indicated under 1, is discussed.
4. A natural inhibitor is isolated from raw Rumanian Dubbs P.D.
5. The effect of this inhibitor is demonstrated on selectively treated gasoline.

In an earlier paper chemical data on the rôle of the time factor in acid treatment of cracked distillates was given.[1]

It follows, from work by Martin, Gruse and Lowy[2] and in reference to above-mentioned paper, that the removal of the conjugated diolefines, in the measure as effected by maleic anhydride, will eliminate the chief cause of gum formation. More complete stabilisation, however, will be obtained only by the removal of unconjugated diolefines and some olefines. The loss a gasoline is suffering by treatment with maleic anhydride is therefore indicating the minimum amount of hydrocarbons to be removed in refining, but does not set the upper limit, if a permanently stable product is desired. It has been shown by the present author that for obtaining a satisfactory copper dish gum test with a given percentage of sulphuric acid, the upper limit is reached after a relatively short contact time and before the reaction between acid and hydrocarbons has come to its natural end.

As shown by Murphy and Wirth,[3] the copper dish test, in spite of considerable adverse criticism during the past few years, still finds favour with the majority of American refiners for routine control and prediction of storage stability. More carefully controlled and reproducible tests are, however, being rapidly developed, and already used to some extent. For determination of actual gum the cold air jet method has been recommended by the Institution of Petroleum Technologists,[4] and the A.S.T.M. are recommending as a tentative standard the high-temperature air jet method B (Committee D-2, 1932).

For the estimation of potential gum a number of proposals, which were particularly well represented at the World Petroleum Congress, 1933, and reviewed by Chilvers,[5] are considering

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accelerated oxidation tests and discussing their correlation to actual storage stability.

The accelerated oxidation test with pure oxygen under pressure and at elevated temperature, due to eventual presence of some less stable hydrocarbons, can still indicate gumming tendency where the copper dish test shows no further gum.

In this paper an attempt is made to give evidence on the effect which the duration of the mixing operation in acid-treating cracked distillates has on the results of an accelerated oxidation test. In parallel with the accelerated oxidation test the corresponding results of copper dish gum tests are reported.

The oxidation test used in this study is the Voorhees and Eisinger test[6] with fixed length of heating time (5 hrs.) and determination of the amount of gum formed. This method, in comparison to the ideal first method described by Voorhees and Eisinger (measurement of the induction period), has the disadvantage of giving only one point of the oxidation curve.[7] It was here given preference merely due to its wider use in oil refineries and the possible correlation of results.

The present investigation has been carried out with a Rumanian Dubbs pressure distillate from flashing operation. Charging stock was a fuel oil residue from a mixture of several crudes (Boldesti, Ceptura, Moreni).

The raw P.D. had the following characteristics :—

Specific gravity		0·766
Acidity (with phenolphthalein)		0·065 mg. KOH/gr.
Dist. A.S.T.M. :—	I.B.P.	28° C.
	100° C.	33·5 per cent.
	150°	54·5 „
	200°	75·0 „
Phenols and carboxylic acids		0·13 per cent. by vol.

These tar acids were determined by extraction with sodium hydroxide (sp. gr. 1·183), following the procedure outlined by Morgan and Meighan.[8]

A 198° C. F.B.P. fraction, obtained from the above material by fractionation, using direct saturated steam and an oil bath for indirect heating, had the following characteristics :—

Specific gravity	0·732
Octane number (C.F.R. Motor Method, A.S.T.M. D 357–33T, 1933)	68·5
Doctor test	Positive
Cold air jet gum	2½
Copper dish gum	270 mg.
Conj. diolefins (with maleic anhydride)	0·5 per cent.
Chemical composition (Egloff and Morrell's method) :—	
Olefines	28·0 per cent.
Aromatic hydrocarbons	23·0 „
Saturated hydrocarbons (paraffins and naphthenes)	49·0 „

Dr. Moser's qualitative silico-tungstic-acid test[9] showed the distillate to be rich in nitrogen bases.

The raw P.D., for the first series of tests (series I), without any previous washing, was directly treated with 2 per cent. by weight of 96 per cent. sulphuric acid in a turbo-mixer rotating at 1500 r.p.m. The mixing time for all experiments was equal to the total contact time. The acid-treated product was centrifugally separated by means of a De-Laval S-N separator the moment the desired reaction time was attained. The mixing time was varied from 5 to 300 seconds. The temperature of reaction was around 20° C. The solution loss of P.D. to acid varied with the reaction time around 1 per cent. by volume.

The acid distillates were washed with water, sodium hydroxide (10° Bé.) and fractionated with the aid of indirect heating and direct saturated steam. The maximum difference in yield on 198° C. F.B.P. gasoline found in this way between the different samples was 2 per cent. The octane number for the sample with the longest mixing time (300 sec.) was 65·5.

The distillates for each particular reaction time, all doctor positive, were divided into three parts and analysed separately; one part without any further treatment, the second part after one wash with sodium hydroxide solution (10° Bé.), the third part after a similar sodium hydroxide wash, followed by a doctor treatment.

The gum tests for the various samples are given in Table I.:—

TABLE I.

Gum Values (mg. gum/100 ml.) for Gasolines F.B.P. 198° C. obtained by Acid Treating P.D. with 2% Acid, Neutralising and Redistillation.

Reaction time (in seconds):	5	10	30	60	120	300
Copperdish test of:—						
Direct distillate	55	20	9	3·5	1	1
Soda-washed distillate ..	20	15	5	2	1	1
Doctor-treated distillate	5	4	3	1	less than 1	less than 1
Voorhees and Eisinger test of:—						
Direct distillate	720	400	360	8	7	3
Soda-washed distillate ..	770	740	730	114	93	4
Doctor-tested distillate	890	860	850	250	120	21

The figures given in Table I. show as a fact that in order to obtain a satisfactory accelerated oxidation test for a given amount of acid, the mixing time has to be longer than was found necessary for the copper dish test, carrying with it a reduction in yield. (Rue and Espach, in *Bureau of Mines Bull.* 333, p. 64, state that stable gasolines are giving, by the Voorhees and Eisinger test, 8 to 40 mg. gum per 100 ml.)

A mixing time longer than strictly necessary for a given gum test is objectionable from the point of view of final yields, and will not necessarily give a better product. In reference to the earlier publication cited above,[1] it might be mentioned here that replacing the complete mechanical separation at the end of the desired mixing time by gravity settling, besides causing an undesirable prolongation of contact time, will leave some of the finest sludge in suspension. The products of the hydrolysis of this sludge by the water-washing operation partly dissolve in the gasoline with known effects.

From Table I. it will be noted that sodium hydroxide and the additional doctor treatment improves the copper dish gum tests of the distillate, while the opposite is true for the Voorhees and Eisinger test results.

In order to give further evidence on the soda-washing effect, another series of tests (series II.) is discussed here. In this series a sodium hydroxide wash (10° Bé.) was applied previous to the acid treatment. All other conditions were the same as described for series I. In Table II. the most characteristic values, *i.e.*, for 60 and 120 seconds' mixing time, are given. This is most characteristic because the respective gasolines, not yet entirely stable to the Voorhees and Eisinger test, were very sensitive to soda and doctor treatment.

TABLE II.

Gum Values (mg/100 ml.) for Gasolines with F.B.P. 198° C. obtained by Soda Washing previous to Acid Treatment referred to in Table I.

Reaction time (in seconds) :	60	120
Copper dish gum test of :—		
Direct distillate	136	100
Soda-washed distillate	49	30
Doctor-treated distillate	16	6
Voorhees and Eisinger gum test of :—		
Direct distillate	40	20
Soda-washed distillate	240	200
Doctor-treated distillate	616	550

Although all gum values in Table II. are considerably higher than the corresponding figures in Table I., the soda and the doctor treatment still results in an improvement of the copper dish gum test and in a reduced stability to the Voorhees and Eisinger test.

By thoroughly extracting samples with distilled water and determining the pH value of the extracts, proof has been obtained that there were no traces of mineral acids or alkalis which could have influenced the results.

That the N-bases present in some raw Californian cracked distillates, and exercising an inhibiting action,[10] were not responsible for the phenomena here observed has been proved by negative

reaction of the treated cracked distillates to Dr. Moser's silico-tungstic-acid test.

From the soda extract obtained during the refining experiments in series II. (soda wash previous to acid treatment) it has, however, been possible to isolate a phenolic inhibitor by precipitation with carbon dioxide. The inhibitor separated readily from the mother liquor. The yield was 0·16 by weight, the specific gravity 1·033 at 20° C., and it gave all reactions for cresols. When treated by some of the methods in use for the separation of the three cresol homologues,[11] it was found to consist chiefly of p-cresol.

The indications received from the figures in Tables I. and II. were verified directly by qualitative reactions and indirectly by adding to certain samples of gasoline :—

1. The natural inhibitor in quantities up to 0·05 per cent. by wt.;
2. Hydrogen sulphide, corresponding to the H_2S content before soda wash ;
3. Various mercaptans in proportions as indicated by their total amount present before doctor treatment, separately or in combinations, corresponding to a reversal of the reactions taking place during the operation of soda washing and sweetening.

For the copper dish gum test it resulted that, although the amount of the inhibitor was of considerable importance (see pre-treatment with soda solution), the soda and doctor treatment of the distillate was beneficial. The accelerating effect of the hydrogen sulphide and mercaptans was more distinct than the inhibiting effect of the amount of natural inhibitor removed by the soda-washing operation.

On the Voorhees and Eisinger test the natural inhibitor has by far the greatest effect. Hydrogen-sulphide was not found to influence the results. The increased gumming tendency after soda washing was merely due to removal of natural inhibitor. Doctor treatment decreased the stability. It is believed that this is chiefly due to the further sodium hydroxide wash, the distillate is suffering under the doctor treatment. Consecutive soda-washing operations have been found to cause a reduction of the gum stability, as illustrated by an example in Table III.

TABLE III.

Effect of Consecutive Soda Washing on Voorhees and Eisinger Test.

	Gum, mg./100ml.
Original sample	320
Shaken for one minute with 2% 10° Bé soda solution	600
Shaken for one more minute with another 2% 10° Bé soda solution	700
Shaken for one more minute with another 2% 10° Bé soda solution	730

The beneficial effect of the doctor treatment in converting accelerating mercaptans like thiophenol[18] into the corresponding disulphides would thus be superseded by further removal of natural inhibitor.

For the sake of completeness it might be mentioned here that none of the samples from Tables I., II. and III. exhibited a positive reaction for peroxides at the time the experiments were carried out.

It has been sufficiently demonstrated for the product under investigation that the results of the gum tests are dependent on the way in which the " sweetening " is carried out. In order to get a desired, controlled effect from the natural inhibitor, it is advantageous to first isolate it from the raw P.D. and to add it to the treated gasoline after the final sweetening has been carried out.

It is most practical to isolate the inhibitor from the sodium hydroxide solution used previous to acid treatment for the removal of hydrogen-sulphide. In practical work, the inhibitor can be precipitated by hydrogen sulphide from still gases[12] by carbon dioxide or waste gases containing appreciable amounts thereof. Spent acid in different forms can also be used.

This natural inhibitor, which can be produced from the waste products of refining, possesses the qualities expected from a suitable anti-oxidant.[13] From commercial inhibitors it differs by its lower effectiveness. Considering the low cost to the refiner, this is, however, no economical disadvantage. The natural inhibitor, discussed above, has been added in quantities from 0·01 to 0·05 per cent. to samples from all final distillates referred to in Tables I., II. and III. Each of those samples could be stabilised to give not more than 10 mg. gum on the Voorhees and Eisinger test and less than 1 mg. on the copper dish test.

Brooks and Parker[14] were the first to demonstrate the presence of phenols and cresols in cracked distillates. Catlin[12] has isolated a tar acid from pressure distillate, which he believes to be methyl-phenylcarbinol $CH_3C_6H_5CHOH$. Klemgard[15] states that a typical crude pressure naphtha contains 0·35 per cent. phenols and cresols. Tanaka and Kobayashi[16] identified the phenolic compounds of a Japanese kerosine from Akita crude. Story and Snow[17] discuss the separation of phenols from petroleum distillates and come to the conclusion that the yield on commercial cresylic acid is too small to be commercially attractive under normal refinery conditions. Hoffert and Claxton[18] give a detailed description of an improved refining method for benzole and also discuss the application of the natural inhibitor (phenols) to benzole. Thomas[19] reports that a series of phenolic natural inhibitors has been isolated

from the soda extract obtained during the refining of Persian cracked gasoline.

Rogers and Voorhees[20] make the following statement, which for the sake of interest is given here in full : ". . . there are certain by-products of petroleum refining and also of wood and coal distillation and of the gas industries, which possess antioxidant properties to a limited extent and which can frequently be obtained at a price sufficiently low to enable them to be considered as anti-oxidants in motor fuel even though their effectiveness is of a relatively low order. Phenolic distillates of wood and coal tar are of this class. There may be a question whether such materials can be added to gasoline in the quantity necessary to give satisfactory gum stability without undesirable side effects. Possibly there is a field for these less effective inhibitors in the more stable gasolines where the amount of stabilisation required is not large."

It has as a fact been possible to show that limiting the attack of the sulphuric acid to the most unstable hydrocarbons, *i.e.*, with reaction time as low as 5 seconds, sufficient prestabilisation is obtained to allow successful application of the natural inhibitor discussed in this paper.

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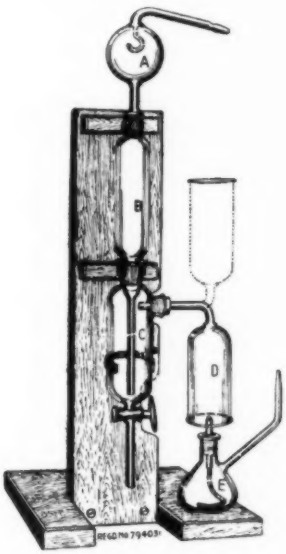
An Improved Form of Sulphur Determination Apparatus.

By Fred Esling, B.Sc., A.C.G.I. (Member).

The apparatus described is a modified form of that previously devised by the author.* In its present form it possesses a number of advantages over the original form. The scrubbing tower (B) is fitted with a perforated glass plate fused into the bottom, and on this rests a quantity of small glass balls which practically fill the tower (B). A small pledglet of glass wool is placed at the top to prevent the balls from falling out when the apparatus is placed



on its side ; the balls and wool should previously be made neutral by boiling in strong HNO_3 and washing well. A catch bulb (A) is fitted into the top of the scrubbing tower by means of a ground glass joint, and a slightly larger tower (C), which is left free of obstruction, fits the lower part of the scrubbing tower also by means of a ground glass joint. This is provided with a stop-cock, and a side opening which carries the glass lamp hood (D) beneath which the lamp (E) is placed for burning.

* *J. Inst. Petr. Techn.*, 1919, **7**, 85.

The method of using the apparatus is very similar to that employed with the older form to which reference should be made. Standard N/16 Na_2CO_3 solution is employed as the absorbent for the acid fumes produced from 10 to 20 ml. being run into the scrubbing tower (B) from a standard burette or pipette. This wets the wool and glass balls, and the surplus runs down the connecting tube and collects in the bottom of (C). Having prepared the lamp in the usual way this is lighted and placed under the hood (D), the products of combustion being drawn through the apparatus by a laboratory water-pump (or other convenient means) attached to the tube outlet from (A). In passing through the standard alkali solution contained in the scrubbing tower (B), the acid produced by the oxidation of the sulphur present in the material burnt is absorbed, thus neutralising a corresponding portion of the alkali which is finally determined. After the test, that is when a predetermined quantity of material has been burnt (or a quantity which can be found by weighing the lamp before and after the test), the apparatus is thoroughly washed out with distilled water, collecting all the washings in a titration flask or beaker. This washing out process can be performed without dismantling the apparatus or removing it from its stand. In practice, the stop-cock is turned on to allow the liquid collected in (C) to run out into the flask (or beaker), and the hood (D) being inverted this is washed down into (C). By closing the stop-cock and attaching a short piece of rubber tubing to the outlet of (A), the washing can be done very effectively by introducing a quantity of water *via* (D) and sucking this up and down in (B) and (C), and then running off into the titration flask. Two or three washings made in this way will be found sufficient. The time occupied in this operation is very short and the apparatus may be used for a further test with very little delay; meanwhile the titration, weighing, etc., may be carried out at leisure whilst the further test is being made. The titration is, of course, done with N/16 H_2SO_4 standard solution and the sulphur content determined by means of the simple relation :—

$$S = \frac{V-v}{W \times 10}\%$$

where V = vol. N/16 Na_2CO_3 used,

v = vol. N/16 H_2SO_4 taken to neutralise.

and W = weight of material burnt.

A weakness in the original form of apparatus was the " U " bend between the two bulbs; this was more often than not the point of fracture, and it will be observed that this has been avoided in the present form. Also, it is a distinct advantage to be able to wash

out the apparatus without dismantling it or removing it from its stand ; breakages are in consequence much less likely. The stop-cock provided at the bottom avoids the possibility of loss by splashing when washing out, a difficulty experienced to some extent in the older form. The lamp is fitted with a " pyrex " tube carrying the wick, and it is possible to replace a damaged tube at slight cost. It will be readily admitted that the time saved in washing out and getting the apparatus ready for a further test is an undoubted advantage.

The Use of the Redwood No. I. Viscometer for the Determination of Viscosity in Absolute Units.

By E. A. Goode, M.Sc., A.A.C.I., and T. V. Heath, A.A.C.I.

Values of viscosity in absolute units are customarily derived from times of flow in the Redwood No. I. Viscometer by means of the conversion equation :—

$$V/D = AT - B/T$$

where V = viscosity in poises ;
D = density of the liquid at the temperature of test ;
T = time of flow in seconds ;
A and B are constants.

The values of the constants A and B are stated as 0·00260 and 1·7 respectively in the 1929 edition of "Standard Methods of Testing Petroleum and its Products," issued by the Institution of Petroleum Technologists. These values are evidently those determined by Higgins of National Physical Laboratory for the N.P.L. standard instrument No. 1307 (N.P.L. Collected Researches, Vol. XI., 1914, 1).

Discrepancies having been observed between results for absolute viscosity as derived from Redwood times of flow by means of the above equation and those obtained by the U-tube viscometer according to British Standard Specification No. 188—1929, it appeared desirable to check the values of the constants in the conversion equation.

The Redwood No. I. Viscometer used in the work had been examined by the National Physical Laboratory in 1925, the N.P.L. report showing that the instrument conforms substantially as to dimensions with the present I.P.T. specification, and stating that an oil having a time of flow of some 6 mins. at 63° F. flowed through it 1·1 per cent. faster than through the N.P.L. standard instrument No. 1307.

An Ostwald viscometer was calibrated by means of several liquids of accurately known viscosity. These liquids were water, 43·3 per cent. solution of ethyl alcohol in water, and 40 per cent. and 60 per cent. aqueous sugar solutions. From the known viscosity of these liquids (taken from British Standard Specification No. 188, of 1929, and International Critical Tables) the equation connecting Ostwald time and kinematic viscosity was determined as :—

$$V/D = 0{\cdot}000729\ T - \frac{0{\cdot}0248}{T}$$

Using this instrument the kinematic viscosities of a number of oils at 25° C. were determined. The times of flow of these oils in the

Redwood No. I. viscometer at the same temperature were then determined.

When the Redwood time of flow is large, the correction term B/T in the conversion equation becomes negligible, the equation approximates to $V/D=AT$, and the graph of V/D against T becomes a straight line whose slope is the value of A.

On plotting the values of kinematic viscosity (V/D) of the above oils against the corresponding Redwood times of flow (T), the graph yields a straight line at the higher values of T, the slope of the line giving the value of A as 0·00248. A point of inflexion on the curve at a time of flow of approximately 50 seconds indicates that turbulent flow commenced at about this point, thus setting a limit to the range of use of the instrument at 50 seconds in contradistinction to the 30 seconds limit stated in the I.P.T. Standard Methods of Testing.

In order to determine the constant B, values of V/DT were plotted against corresponding values of $1/T^2$ after the method of Higgins (*ibid.*).

If the equation $V/D=AT-B/T$ be valid, the graph should be a straight line, the slope of which is the value of B and the intercept of which on the V/DT axis is the value of A.

In the present case, instead of a straight line a curve was obtained, the slope of which decreases with increasing values of T from 50 seconds upwards, indicating that the customary form of conversion equation is not applicable to the instrument in question.

With the value 0·00248 for A as determined above from the higher times of flow, it is possible by modifying the correction term to derive an equation fitting the results over the useful range of the instrument, *i.e.*, for times of flow of 50 seconds and upwards. The equation so derived is $V/D=0{\cdot}00248T-182/T^{2{\cdot}15}$.

Redwood time seconds.	Kinematic viscosity. Calculated from Redwood times. I.P.T. equation.	Modified equation.	Determined by Ostwald viscometer.
57·6	0·120	0·113	0·113
68·0	0·152	0·148	0·148
95·0	0·229	0·225	0·226
171·0	0·435	0·421	0·424
224·0	0·575	0·554	0·562
280·5	0·723	0·695	0·695
538·0	1·40	1·33	1·35
732·5	1·90	1·82	1·80

As shown by the table above, this equation gives values of kinematic viscosity derived from Redwood times of flow in close agreement with the results of determinations by the Ostwald viscometer. Results calculated by the application of the I.P.T. equation to the Redwood times are shown for comparison.

Allowing for the 1·1 per cent. difference in time of flow between the Redwood viscometer employed and the N.P.L. standard instrument, the above results show the Higgins value for A to be 5·9 per cent. too high. This result is in fair accord with the statement of Barr (Aero. Research Committee, Reports and Memoranda, No. 906, March, 1933) that the Higgins value gives results 5 per cent. too high.

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The Non-Carcinogenicity of Certain Synthetic Lubricating Oils and the Action of Some Commercial Spindle Oils, Solvent-Fractionated Spindle Oil Distillates and Tar Oils, Tested under Similar Conditions.*

By D. L. Woodhouse, Ph.D., A.I.C.†

Summary.

1. In the mouse tests described, synthetic lubricating oils produced from ethylene in presence of anhydrous aluminium chloride at temperatures up to 150° C. exhibited *no carcinogenic* properties. The oils represented hydrocarbon series including olefinic, naphthenic and polynuclear naphthenic types.

2. In the case of a sulphur dioxide-treated, paraffin base, *unrefined* spindle oil distillate, the carcinogenic constituents were concentrated in the sulphur dioxide extracts, especially the second extract.

3. It is considered that where mouse tests indicate only slight carcinogenic action the results of such mouse tests are more difficult to correlate with human tendencies to cancer than where mouse tests are *strongly positive or entirely negative.*

During recent years a number of neoplastic diseases have been recognised among workers in certain industries subsequent upon the conditions of their employment which are referred to as occupational cancers.

Such include the disease of the bladder occurring among certain branches of chemical workers and attributed to the effect of long-continued exposure to aniline and allied compounds,[1,2] the skin carcinomas of the tar industries,[3] and the epitheliomas occurring among shale oil workers.[4] During the years 1923–1928 over 400 cases of epitheliomatous ulceration[5] were notified among workers coming into contact with mineral oils chiefly in connection with mule spinning, in which industry 140 deaths were ascribed to this cause.[6]

The recent researches of Kennaway and his co-workers[7] have proved it not improbable that the carcinogenic properties of coal tar and similar products are due to the influence of small proportions of poly-benzene constituents,[8] one of which, 1 : 2 benzpyrene, has been isolated from coal tar[9] and also synthesised and proved to be strongly carcinogenic to mice[10] as well as rats and fowl. Besides having the capacity of inducing malignancy by external application, sarcomas have also been produced by injecting into muscular tissues, which give rise to secondary growths and are trans-

* This work has been carried out under the auspices of the British Empire Cancer Campaign (Birmingham Branch). Paper received, March 14th, 1934.

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plantable.[11,12,13] These hydrocarbons have a blue-violet fluorescence,[14] specially visible in ultra-violet light yielding spectra with characteristic bands. It is of interest, therefore, to note that tar oils, spindle and shale oils, which show carcinogenic properties, are also strongly fluorescent.[8]

On the other hand, many pure organic compounds such as naphthalene, cyclohexane, fluorene, anthracene, the saturated paraffins and medicinal paraffin[7] have been tested very carefully and found to have no carcinogenic action.

It has generally been agreed among experimental cancer investigators that in the case of tar and allied products, those fractions or constituents which have been subjected to temperatures over 400° C.[15,16] are most potent in the production of animal tumours; thus, horizontal retort tar produces a larger proportion of epitheliomatous warts in mice and induces the cancerous phase in a shorter time than vertical retort tar (unpublished experiments from this laboratory). The low carcinogenic action of petroleum oils compared with tar distillates is, therefore, probably due in part to the fact that their heat treatment is moderate.

It is also agreed that poly-nuclear aromatic compounds are more carcinogenic than open chain compounds, and that unsaturated compounds[17,18] are more potent than the saturated series. The possible activity of sulphur compounds has not been definitely proved, although the irritant action of such compounds as " mustard gas " is well known. In the case of this substance it has been demonstrated that, in conjunction with coal tar products, its application results actually in a diminished number of epithelimas.[19]

Up to the year 1931, when the investigations reported in this paper were begun, most of the studies in experimentally induced tumours had been carried out with complex mixtures such as tar extracts and distillates. When, therefore, attention was drawn to the very interesting series of synthetic lubricating oils produced by Nash, Stanley and Bowen,[20] it was considered that they afforded a unique material for testing with regard to their action on mice for the following reasons :—

1. They had been produced from a single pure organic compound of low molecular weight and known structure, namely ethylene.
2. Their synthesis involved comparatively low temperatures and consisted of polymerisation by pressure in the presence of aluminium chloride to compounds containing from 10–50 carbon atoms per molecule.
3. The chemical and physical properties of these oils were described.

Details of Oils Tested.

The following fractions of oils were selected as representative of the lubricating fractions obtained from the synthetic processes described.[20]

Sample No. 1.—A clear liquid containing hydrocarbons of series C_nH_{2n} and naphthenic in character, boiling at 120–140° C. at 10 mm. It was fraction 7 Expt. 32, in which ethylene was treated with powdered aluminium chloride (without any liquid diluent) at 150° C. in a 2 litre autoclave at 55 atmospheres pressure for six hours, yielding 210 gm. of crude oil. This fraction had the following characteristics :—

D_4^{20} 0·8319, N_D^{20} 1·4630. Mol. wt. 212.

Unsaturated hydrocarbons were absent from this oil.

Sample No. 2.—This was fraction No. 12 from the above experiment, boiling at 220–250° C. at 10 mm., and contained hydrocarbons of general constitution C_nH_{2n-10}, and was thus of polynuclear naphthenic type. Its characteristics were :—

N_D^{20} 1·5296. Mol. wt. 350.

Approx. formula $C_{26}H_{42}$.

Sample No. 3.—This oil was fraction 7A of Expt. 45–50 obtained from the product of ethylene polymerisation conducted at 10–15° C. with average pressure of 40 atmospheres in presence of 100 gms. of aromatic free petrol ether. This fraction boiled between 225–250° C. and had the following characteristics :—

D_4^{20} 1·4622. Mol. wt. 384.

Approx. formula $C_{28}H_{56}$—Naphthenic (C_nH_{2n}) in type.

The above oils were type "A" oils—*i.e.*, they were in free condition as contrasted with the two following samples which were the type "B" oil which were found in combination with aluminium chloride and from which they were freed by the action of water.

Sample No. 4.—This oil was from the "B" type product from the above experiment after separation from the aluminium chloride complex. It was fraction 8B and was olefinic in character : formula C_nH_{2n} with a proportion of C_nH_{2n-2}. Its unsaturated character was shown by its iodine number.

Sample No. 5.—Also a "B" type oil obtained as fraction 4B of the same experiment using a solvent. It distilled between 150–175° C. at 10 mm. and had the following constants :—

D_4^{20} 0·8451. N_D^{20} 1·4795. Mol. wt. 262.

Bromine number between 35–40.

It was a viscous brown oil containing olefinic hydrocarbons of series C_nH_{2n} and C_nH_{2n-2}.

Control.—In case slight traces of aluminium chloride were present in these synthetic oils and might exert a carcinogenic action, a control experiment on mice was conducted with an innocuous oil containing traces of this substance.

A sample of pure powdered anhydrous aluminium chloride was shaken with liquid paraffin (medicinal), and the upper layers of oil removed and used for application to a series of mice.

Applications were made in a similar fashion and for the same period of time.

However, no neoplasms were produced by this aluminium chloride-treated oil.

Experimental Technique of Animal Tests.

In order to ascertain whether these oils had the power of producing epitheliomas, white mice were epilated with sodium sulphide solution over an area as large as a shilling in the scapula region on the back and the oil applied by means of a small tube twice weekly. Further epilation was done after approximately 3 months; the hair grew slowly, probably owing to the influence of the oils.

External application in this manner was adopted since it has been found very difficult to produce neoplasms by subcutaneous injections of oils.

The animals were housed separately in glass vessels with perforated zinc tops and fed on mixed diet containing crushed oats, whole wheat, Melox meal and milk. They maintained vigorous health during the tests, which were continued for over 18 months, and mortality from disease was very low.

A total of 72 mice were used on these experiments.

Experimental Results.

It was found that in the whole series of synthetic oils tested not one malignant growth was produced. On histological examination the skin showed no definite change from the normal condition except slight thickening in some cases. A single exception was the appearance of a papilloma on an animal painted with Specimen No. 5. This was small and did not develop any malignant properties, and was probably quite adventitious.

The non-carcinogenic properties of these samples is in keeping with the fact that they were produced at relatively low temperatures. Probably the work of Twort and Fulton,[17] who produced carcinogenic synthetic tars from pinene and turpentine, and of Kennaway,[7] who, having tested the products yielded by isoprene, acetylene and cholesterol at 700–920° C., continued to observe the properties of the substances formed at lower temperatures from tetra-hydro-naphthalene (tetralin) in presence of aluminium

chloride approximates most closely to these experiments. In this instance, however, carcinogenic fractions were obtained, for, by using the clear, reddish-brown, viscid residue obtained from the interaction at 37° C. the latter produced 8 cancers in 20 mice in 256 days. The variability of commercial tetralin gave difficulty in reproducing the exact materials. Some experiments of Hieger are also referred to in the same communication. In these, carcinogenic substances were obtained by the action of aluminium chloride on acetylene at room temperature, the products being extracted by boiling benzene. The products obtained by the action of aluminium chloride on xylene were also feebly carcinogenic. It is not unlikely that the condensation products of acetylene are of a more complicated nature and probably more unsaturated structure than these obtained from ethylene.

The behaviour of fractions from crude petroleum oil under comparative conditions is of interest. An unrefined spindle oil distillate from a crude oil of paraffin base was given two successive washes with an equal volume of liquid sulphur dioxide, the products being :—

Oil	C.1	Unrefined spindle oil distillate
,,	C.2	Raffinate
,,	C.3	First SO_2 extract
,,	C.4	Second SO_2 extract

TABLE I.

Properties of Petroleum Fractions.

Oil.	Viscosity at 140° F. (seconds Redwood)	Sp. Gravity.
C.1	49·5	0·903
C.2	46·5	0·869
C.3	110·0	1·045
C.4	86·5	1·021

These distillates were used in mouse tests giving the following results :—

TABLE II.

Oil.	No. of mice utilised.	Approx. duration of test.	No. of neoplasms.	Percentage of neoplasms.
C.1	30	12 months.	2	6·6
C.2	25	,,	0	—
C.3	52	,,	6	11·5
C.4	57	,,	10	17·6

It was thus obvious that the carcinogenic bodies from the unrefined distillates were concentrated in the sulphur dioxide extracts, the second extract causing more neoplasms than the first. It should be noted that these oils were in no case marketed products but specially prepared unrefined distillates. The chemical

and physical-chemical refining of well-refined spindle oils before being placed on the market would remove practically all the more reactive constituents.

It must be pointed out that correlation of results of mice tests and human liabilities to develop epitheliomas is still somewhat difficult. This correlation appears to be more possible in the case of substances of *negative* carcinogenicity, such as the synthetic oils referred to in this paper, medicinal paraffin and sulphur dioxide refined petroleum spindle oil, and in the case of fairly strongly carcinogenic substances—*e.g.*, certain coal tars. With the latter, mice tests indicate malignant growths in as short a period as 28 weeks.

The results obtained from a series of animals from a similar stock, using : (1) a horizontal retort coal tar ; (2) petrol ether extract of pitch, and giving applications in similar fashion, are shown in Table III.

The pitch extract was produced by distilling horizontal retort coal tar up to a temperature of 400° C., powdering the residue and refluxing 100 gms. with 200 ml. petrol ether (B.P. 60–80° C.) for 30 mins. The clear, amber coloured liquid was applied by means of a camel hair brush.

TABLE III.

Tar.	No. of animals.	Approx. duration of applications.	No. of neoplasms.	Percentage of neoplasms.
Horizontal Retort Coal Tar ..	34	28 weeks.	24	70
Pitch Extract	24	40 ,,	19	79

It can be definitely stated that much longer applications of the petroleum oils were necessary to produce warty growths than in the case of the coal tar and extracts. The percentage of warts in the case of petroleum oils is also very much lower, and of malignant growths still more so. Moreover, in the tar experiments a number of secondary cancers (lungs) were observed.

There appears to be some difficulty in correlating the results of mouse tests and human tendencies in the case of substances such as petroleum oils that produce only a few neoplasms among a large number of mice treated. As an example of this difficulty of correlation, the case of two commercial spindle oils is illustrative. Two oils were selected respectively from the stocks of : (*a*) a spinning mill where no cases of mule-spinners cancer had been recorded, and (*b*) a mill where six cancers had recently been reported. Mouse tests indicated slight carcinogenic properties in the case of the two oils, but a greater carcinogenic action on mice of oil (*a*) than oil (*b*).

The Author wishes to express his thanks to Sir Gilbert Barling for his interest in this work; to Professor A. W. Nash, for the synthetic and petroleum oils tested, and to the Anglo-Persian Oil Company, Ltd., for a grant which covered the cost of the animal experiments.

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REVIEWS.

PETROLEUM DEVELOPMENT AND TECHNOLOGY, 1934. NEW YORK, AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS, 1934. Pp. 458. $5.

The annual volume of transactions read before the Petroleum Division of the American Institute of Mining and Metallurgical Engineers at their October, 1933, and February, 1934, Sessions, constitutes a complete review of the oil production situation in the U.S.A. A summary of the production position in each of the major oil producing countries of the world is also included.

As in past years the information contained in this volume is of the greatest interest to all classes connected with oilfield operation, and particularly to those whose activities are concerned with the economics of the Industry. The bulk of the papers delivered this year deal with Stabilisation, Economics and Production, both Domestic and Foreign, and less space than usual is devoted to Production Engineering Research. It is usually possible at these Congresses to discern an underlying theme and Sub-Surface Data occupies that position this year.

The papers on Engineering subjects are to be found in Chapter I., and an outstanding contribution is the paper on "Properties of Hydrocarbon Mixtures as Related to Production Problems," by Professor W. K. Lewis. The data obtained will undoubtedly enable a better understanding of the behaviour of deep reservoirs and definitely emphasises the need for fundamental research along these lines. Directional Drilling, Instruments for Recording Sub-Surface Data and Formation Testers are dealt with, but unfortunately less fully than might be hoped for by those unable to obtain detailed information on such topics. Other papers of interest to the Petroleum Engineer deal with such subjects as the Theoretical Analysis of Water Flooding Networks; Basic Data for Oil and Gas Wells; Effect of Gas Withdrawal upon Reservoir Fluids; a New Method for Measuring Vented Gas; Comparative Resistance of Certain Commercial Ferrous Materials to Corrosion by Gaseous Hydrogen Sulphide. The paper dealing with water flooding is a summary of one of the Institute's Technical publications, and gives the results upon which the author's conclusions were based. The mathematical details of the original paper have been omitted from the abridged form.

Five articles are devoted to Economics dealing with such subjects as Consumption of Petroleum Products and transportation as a factor affecting the present and future development of the Oil Industry.

The chapter on Stabilisation is admirably introduced by the Chairman of the Stabilisation Committee of the Institute and of the other papers presented that by Dr. Umpleby will, perhaps, be of most interest. The Kettleman Hills Middle Dome project is dealt with in the other paper in this section. Dr. Umpleby has summarised the existing information on reservoir energy and its efficient utilisation, and has emphasised the necessity for flexibility in laws and regulations due to the probability that the relative importance of controlling factors will change with advancing knowledge.

A review of the Developments in Refining Engineering during 1933 is given, and the remainder of the volume is devoted to statistics of oil and gas production in the various States in the U.S.A. and in all the other major oil producing countries of the world.

All the papers in this volume are authoritatively written, and credit is due to the compilers for the manner in which they have been presented. The work can be highly commended, and should be possessed by all interested in the Petroleum Industry.

L. V. W. CLARK.

DAS SCHROTBOHREN. Dr. ing. Josef Kern. Leoben (Steiermark), Ludwig Nuessler, 1933. Pp. 178. Paper cover, Sch. 8; bound, Sch. 11.

Although boring by means of the chilled shot method is not a usual practice in the petroleum industry, yet it is much used in mining and water supply work, and the excellence of the cores obtained render it worthy of notice. Very little has been published concerning the subject, and any attempt to fill that gap in the literature should therefore be welcome.

The author divides his subject matter into five sections. The first section is more or less introductory in character, its most important point being a discussion on the manner in which the shot acts on the surface of the rock, the author attempting to endorse his viewpoint by a mathematical consideration of the relation between the pressure of the shot on the rock surface and the physical properties of the rock. In the second section a description of the rig and various appliances used in shot boring is given. In his treatment of the methods by which shot is introduced into the borehole, and in his description of the tools, the author is clear and keeps well to the point. The question of pumps might be more fully discussed, however, whilst in the chapter on the rig and derrick it would have been an advantage had he approached the subject directly rather than by a discussion on rotary rigs in general and diamond drilling and combination rigs in particular. The process of drilling occupies the whole of the third section, and here again the treatment is clear and good, although one could wish that it were wider in scope, especially with regard to fishing operations and methods used in overcoming difficulties in drilling. However, too full a treatment can hardly be expected in a book of 178 pages, and particularly since the author states that the book is more in the nature of an introduction to the subject. The last two sections occupy but a few pages, and deal with maintenance and suggestions for research work on the action of the shot and best operating conditions. They might be expanded with advantage. S. E. COOMBER.

CHEMISTRY OF PETROLEUM DERIVATIVES. Carleton Ellis. New York Chemical Catalogue Co., 1934. Pp. 1285. $18.

This really monumental work reflects the greatest credit on the knowledge and industry of Mr. Carleton Ellis, whose reputation as a petroleum chemist stands so high in all parts of the world.

Mr. Ellis points out that during the last ten years the chemists interested in petroleum technology have maintained that the numerous hydrocarbons abundantly available in the product of our oil wells will ultimately provide the basis of a new organic chemical industry, yielding new substances in at least as great a variety and of the same essential utility as the products of coal tar. Notwithstanding the extraordinary difficulties of separating pure chemical individuals from the highly complicated mixtures that occur in crude oil, there is already in existence a vast amount of information on the behaviour of some of the individual hydrocarbons in petroleum. The difficulties in the collation of the widely diffused literature in this field are almost insurmountable, but Mr. Carleton Ellis for some years past has been accumulating material and has now made it available to chemists at large.

The Author calls attention to the pessimistic view held by some of his contemporaries on the consummate difficulties brought about by virtue of isomerism of the hydrocarbons, and shows that a paraffin of 9 carbon atoms could be represented by 35 isomers and 55 if stereo-isomers are included, and that one of 20 carbon atoms would have 3,395,964 possible isomers. Whilst it is a matter of common knowledge that a multiplicity of isomers exists, it is simply improbable that anything like such a complicity could be assumed.

But, in spite of these difficulties, progress is very slowly and steadily made, both scientific and technologic. In fact, technology has shown a more rapid progress than scientific knowledge.

The Author himself has been foremost in the conversion of olefines from cracked products into commercially valuable material, and by virtue of this pioneering work, he is most admirably equipped to deal with the many complications of syntheses from hydrocarbons.

The book, in its 1285 pages, is a veritable encyclopædia and the mass of material concerned with the development and utilisation of the derivatives of natural gas and petroleum will be indispensable to technologists at large. It really stands in a definite class by itself by reason of its extraordinary comprehensiveness.

The account of the fundamental chemistry of cracking, of the derivatives of ethylene and of polymerisation is authoritative and bears the imprint of real personal knowledge of the subjects. It would be impossible to detail even the chapter headings, but they can be summarised as follows :—

> Cracking and pyrolysis of hydrocarbons, including production of olefinic and aromatic derivatives; conversion of olefines to alcohols, including the higher secondary and tertiary alcohols, esters and other materials; sulphur derivatives; general reactions of olefines; polymerisation; halogenation; nitrogen compounds; oxidation products; sulphonated products; naphthenic acids; and methods of analysis.

In every one of these fields there is a carefully compiled bibliography—in fact, a reasonably complete reference library for those working on petroleum chemistry.

The indexing should be specially commended. The name index runs to 29 three-column pages, the subject index to 101 two-column pages. The patent references are, so far as one can check up, remarkably complete.

Frequently a reviewer, impressed with the authoritative way in which a book before him has been produced, is inclined to say "This work is indispensable." In no case within your reviewer's knowledge is that statement more true than in Carleton Ellis's stupendous compilation.

A. E. DUNSTAN.

CHEMISCH-TECHNISCHE ENTWICKLUNG AUF DEM GEBIETE DER KOHLENWASSERSTOFFÖLE, 1928–1932. Dr. M. Pflücke. Berlin, Verlag Chemie G.m.b.H., 1934. Pp. xviii.+695. In paper cover RM. 58, bound RM. 60.

A comprehensive summary of literature and patent specifications published during the years 1928-1932 and covering all phases of the treatment of petroleum and petroleum products, including physical and chemical properties and analysis. Each reference is complete with a short abstract of the scope of the article or patent, and there is a numerical index to the patent specifications, which are from nineteen countries. An excellent subject index is provided, and it is to be regretted that there is not also an author index. Apart from this one drawback, the book should prove a useful reference volume to those who wish to trace work on the refining and treatment of petroleum during the period covered.

THE SIGNIFICANCE OF TESTS OF PETROLEUM PRODUCTS. A.S.T.M., Philadelphia, 1934. Pp. 76, $1.

This report, which has been compiled by Committees D–2 and D–4 of the American Society for Testing Materials, is an extensive revision and amplification of the first edition which appeared in 1928. Since that date many tests have been perfected and new ones brought out, and full cognizance has been taken of the general advancement in petroleum technology.

The choice and interpretation of tests for petroleum products is of great importance, and the authoritative information given in this book will be of the utmost value.

All the methods standardised by the A.S.T.M., as well as others which are pertinent, are discussed.

A.S.T.M. Standards on Petroleum Products and Lubricants. A.S.T.M., Philadelphia, 1934. Pp. 340, $1.75.

The 1934 edition of the annual publication, dealing with the methods of test standardised by Committee D–2 of the American Society for Testing materials, contains 53 test methods in their latest form. A number of tentative and standard methods have been revised, including sulphur by the lamp and bomb methods, colour of lubricating oil and petroleum by A.S.T.M. Union Colorimeter, cloud and pour point, tests for emulsified asphalts and the abridged volume correction table.

Two new tentative methods are published, one for gum content of gasoline and the other for separation of liquid asphaltic products.

Tentative specifications are given for fuel oils for oil-burning equipment and for five types of emulsified asphalt (coarse aggregate plant mixes, retread and coarse aggregate mixes, heavy premix-summer grade, heavy premix-winter grade, quick setting).

The 1934 report of Committee D–2 includes interesting discussion of the work on various tests for gasoline, and a classification for Diesel-engine fuel oil.

Tentative definitions of terms relating to petroleum and to materials for roads and pavements are given.

World Petroleum Directory, 1934. London, World Petroleum, 1934. Pp. LI.+578. £2 2s. 0d.

The second annual edition of the World Petroleum Directory contains detailed information regarding the oil companies operating in various parts of the world.

The Progress of Science, being an account of recent fundamental researches in Physics, Chemistry and Biology. J. G. Crowther. London, Kegan Paul, 1934. Pp. 304.

It is becoming a matter of greater and greater difficulty for the intelligent man in the street to get even a faint idea of the remarkable developments of current scientific research. And thus it has become very necessary to have an interpreter, who in the simplest possible fashion can indicate to the intelligent reader what actually is happening in the various laboratories of the world.

Mr. Crowther has already shown very notable ability in this direction and the volume before us strengthens our belief in his capacity to put in an easy form, yet accurate, the highly complicated matters about which he writes.

In his preface he justly draws attention to the fact that a knowledge of science is now necessary in every person who wishes to take an intelligent interest in human affairs and that political and industrial leaders can no longer leave problems involving scientific knowledge to technical experts, they must try to form their own opinions, and if they do not, they become victims of false theories.

The book contains in its nine chapters an account of that highly complicated matter—Modern Physics. The work for which the Cavendish Laboratories

are so famous is described from the angle of the continuity that has been maintained in its epoch-making researches. It is a matter of common knowledge that the results that have hitherto been obtained in this laboratory are of fundamental importance and have led to the development of the latest views on the structure of matter. There follow chapters on the work at Copenhagen on the quantum theory, physical researches in progress in the Soviet Republic, the Expansion of the Universe and the theory of stellar evolution and of the cosmic rays. Thus, more than one-half the book is concerned with the development of physical theory.

The author then proceeds to describe diplogen ("heavy hydrogen") and its importance in chemical theory and thus pays tribute to American investigators.

He completes his survey by a chapter on the chemistry of evolution, on human hereditary and on pernicious anæmia.

This brief list of contents will indicate the width of Mr. Crowther's survey. To the technical man immersed in his day-by-day problems, it will be a revelation to proceed with Mr. Crowther into territory outside his normal experience. He will find lucidity and ease of exposition, and although in places the reading is by no means light, yet the effort of understanding will be amply recompensed. To the ordinary intelligent reader, other than one engaged in technical pursuits, the book will be found stimulating and vastly interesting—more particularly the biological side will attract him.

The remarkable success of Sir James Jeans' interpretations indicate that there is a very considerable public that is not satisfied with a mere facile statement of results. The public wishes to know how the results were obtained. Mr. Crowther's very excellent historical method will be highly appreciated.

A. E. DUNSTAN.